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SOME REACTIONS OF SILICON COMPOUNDS

by

R. SHILTON, M.Sc.

A THESIS

**Submitted to the Faculty of Graduate Studies in Partial
Fulfilment of the Requirements for the
Degree of Doctor of Philosophy**

**Essex College,
Assumption University of Windsor
July, 1963.**

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ABSTRACT

Attempts to prepare compounds containing a carbon-silicon double bond by pyrolysis of silyl hydrogen phthalate esters gave instead phthalic anhydride and a silanol. Reaction between a chlorosilane and sodium triphenylmethyl gave coupling products as the only identifiable silicon-containing material, in accordance with the experience of previous authors. Hydrogen phthalate esters of tertiary alcohols reacted with bromine to eliminate phthalic acid and form a vicinal dibromide or its dehydrobromination product. The reaction was fast in the case of alcohols with a phenyl group attached to the α -carbon atom. In attempts to extend this reaction to silyl hydrogen phthalates there appeared to be no reaction with esters of alkylsilanols and in those of arylsilanols the aryl groups were detached as readily as phthalic acid was eliminated.

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It is a pleasure to thank Dr. K. G. Rutherford of this University for suggesting and supervising this problem.

TABLE OF CONTENTS

	Page
ABSTRACT.	ii
ACKNOWLEDGEMENTS.	iii
LIST OF TABLES.	vi

Chapter

I. HISTORICAL SURVEY

Introduction.	1
Preliminary Discussion of Theoretical Considerations.	2
Early Attempts to Prepare Carbon-Silicon Double Bonds and their Analogues.	8
The Work of Fritz and Grobe	15
The Work of Benkeser.	21
Other Attempts.	24

II. THEORETICAL CONSIDERATIONS

Evidence for Participation of Silicon in Resonance Forms	25
Siliconium Ions	36
Current Theoretical Considerations.	38
Preparation of Carbon-Carbon Double Bonds by Pyrolysis of Hydrogen Phthalates of Tertiary Alcohols	41

Chapter	Page
III. DISCUSSION OF EXPERIMENTAL RESULTS	
Silyl Esters.	45
Present Attempts to Prepare Silyl Hydrogen Phthalates and Pyrolysis thereof.	47
Hydrolysis of Chlorosilanes	48
Trimethylsilyl Hydrogen Phthalate	54
Preparation of Silyl Benzoates.	56
Reaction of Tertiary Carbinyl Hydrogen Phthalates with Bromine	58
Attempted Extension to Silicon Series	65
Attempted Reaction of Silyl Benzoates with Bromine	69
Reactions of Chlorosilanes with Sodium Triphenylmethyl	70
Resume and Conclusions.	73
IV. EXPERIMENTAL PROCEDURES	74
REFERENCES	129
VITA AUCTORIS	136

LIST OF TABLES

Table		Page
I.	Dipole Moments (Debye Units) of Chlorosilanes and Chloromethanes	35
II.	Moments of Me_3Si Group in $p\text{-XC}_6\text{H}_4\text{SiMe}_3$.	36

CHAPTER I - HISTORICAL SURVEY

Introduction

The object of this work was to investigate some possible routes to the formation of compounds containing a silicon atom doubly bonded to carbon. The preparation of such compounds had previously been claimed by only three groups of workers, but in no case had the claim been substantiated. During the course of the present work another claim was made but appears to have been erroneous. Two other authors have reported the preparation of aromatic systems containing silicon but have now withdrawn their claims. (For references to the above claims see below.) It may therefore be said that to date no compound containing a carbon to silicon double bond has been prepared. Theoretical considerations bearing on the possibility of forming such bonds are discussed below.

A compound containing a carbon to silicon double bond, if preparable, would be of considerable theoretical interest. One would like to know whether it had the usual properties of an unsaturated linkage, such as ability to add

halogens, ease of hydrogenation, and reaction with potassium permanganate. The compound would also be of interest as a possible starting material for the preparation of polymers analogous to those so fruitfully developed in the carbon series.

Preliminary Discussion of Theoretical Considerations

The work of Kipping and his school, extending over many years^{*}, was directed toward showing the many analogies between the silicon series and the carbon series. Nevertheless, the analogy proved to be only partial. The list of pure compounds containing silicon is very brief by comparison with that of organic compounds. Only a few compounds containing only silicon and hydrogen are known, in contrast to the very large number of hydrocarbons, and evidence for structural isomerism among silanes is almost nonexistent. Furthermore, several important classes of compounds have no representative in the silicon field. In particular, there is no evidence for the existence of $\text{Si}=\text{O}$ groups, and hence no silicon analogues of such compounds as aldehydes,

^{*}For a complete list of papers see "An Introduction to the Chemistry of the Silicones", E.G. Rochow, John Wiley and Sons, New York (2nd edn.) (1951) p. 76.

ketones, acids, and esters. Even among silicon compounds formally analogous to carbon compounds there are considerable differences in behaviour. For example, esters of the type $\begin{array}{c} | \\ -\text{Si} \cdot \text{CO} \cdot \text{OR} \\ | \end{array}$ lose carbon monoxide on heating¹ with formation of $\begin{array}{c} | \\ -\text{SiOR} \\ | \end{array}$, an ether-type compound. This reaction has no parallel in the carbon field. Silanols condense forming siloxanes containing the group $\equiv \text{SiOSi} \equiv$ much more readily than alcohols condense to form ethers^{2,3,4}. The reaction is catalysed by both acids and bases and indeed special techniques are required (e.g.^{5,6}) if the uncondensed silanol is to be prepared. Silane diols (e.g. diphenylsilanediol) and even triols⁷ are known and, though they are readily dehydrated to polysiloxanes, they are much more stable than their carbon analogues.

¹A.G. Brook, J. Am. Chem. Soc., **77**, 4827 (1955).

²F.S. Kipping, J. Chem. Soc., (1927), 105.

³R.O. Sauer, J. Am. Chem. Soc., **66**, 1707 (1944).

⁴W.T. Grubb, J. Am. Chem. Soc., **76**, 3408 (1954).

⁵C.A. Burkhard, in "Inorganic Syntheses", vol. III, p. 62.

⁶L.H. Sommer, E.W. Pietrusza, and F.C. Whitmore, J. Am. Chem. Soc., **68**, 2282 (1946).

⁷Toshio Takiguchi and Fumio Hirata, Kogyo Kagaku Zasshi, **62**, 435 (1959) - cf. Chem. Abs., **57**, 8603 (1962).

On the other hand there remains a large area over which carbon and silicon show great similarity. Although some ions exist in which silicon exhibits a valency of 6, the best known being the hexafluorosilicate ion, SiF_6^{--} , in which the six fluorine atoms are disposed octahedrally about the silicon atom⁸ and although it is probable that silicon can exhibit a covalency of five in the transition state⁹, in its stable compounds it always exhibits a covalency of four, as does carbon. Moreover the stereochemistry is tetrahedral as has been shown by an X-ray diffraction study¹⁰ of SiI_4 and by resolution¹¹ of silicon compounds (which indicates only a non-planar structure). This behaviour would be expected since the electronic structure of a carbon atom is $1s^2 2s^2 2p^2$ and of a silicon atom is $1s^2 2s^2 2p^6 3s^2 3p^2$. One would expect the treatment so successfully applied to carbon by Pauling and Slater would be equally applicable to silicon.

⁸J.A.A. Ketelaar, Z. Kristallog., 92, 155 (1935).

⁹C.G. Swain, R.M. Esteve, and R.H. Jones, J. Am. Chem. Soc., 71, 965 (1949).

¹⁰O. Hassel and H. Kringstad, Z. Phys. Chem., B13, 1 (1931).

¹¹a) F.S. Kipping, J. Chem. Soc., (1907), 209.
 b) F.S. Kipping, J. Chem. Soc., (1908), 457.
 c) C. Eaborn and C. Pitt, Chem. and Ind., (1958),

That is, a 3s electron would be promoted to a 3p orbital making the valency shell $3s3p^3$. These electrons would then be hybridised to four equivalent tetrahedrally disposed sp^3 orbitals. There is, however, an important difference between silicon and carbon. In the latter, the lowest-lying unfilled orbitals are 3s in the next shell, whereas in the former the 3d orbitals are reasonably close in energy to the 3p orbitals, giving rise to the possibility that sp^3d^2 hybrid orbitals might be used. These are doubtless the orbitals used in the SiF_6^{--} ion. However, it seems certain that in the simpler tetravalent compounds of silicon the orbitals used are indeed sp^3 hybrids.

Two theories of the carbon-carbon double bond are currently in use. In one, the carbon atoms are taken to be tetrahedrally hybridised and two pairs of orbitals (one from each atom) are taken to be overlapped so as to give two 'bent bonds' in which the overlap of each pair is less than in a single sp^3-sp^3 carbon-carbon bond but the total overlap of the two pairs, while less than that of two single bonds, is greater than that of one single bond. In the other model the carbon atoms are described as having one s and two p electrons hybridised to form an sp^2 trigonal hybrid orbital with the remaining p orbital unhybridised and having its nodal plane in the plane of the three sp^2 orbitals. A pair of sp^2 hybrid

orbitals, one from each atom, is then overlapped to form a σ bond of cylindrical symmetry. The two unhybridised p orbitals, being of the same symmetry, can then overlap to form a π bond of symmetry characterised by the presence of a nodal plane in the plane of the σ bond and the four other sp^2 hybrid orbitals.

The two above models are not as dissimilar as appears: Pople's equivalent orbital treatment¹² shows that the second is very similar to the first when the σ and π bonds are replaced by their equivalent orbitals. Nevertheless there are differences to be expected between the two models. From the first, or bent-bond model, one expects the X-C-Y angle in $\begin{array}{c} X \\ \diagdown \\ C \\ \diagup \\ Y \end{array} =$ to be approximately tetrahedral, or $109^\circ 28'$, and from the second to be approximately trigonal, or 120° . In each case these figures would be modified by environmental and steric factors. The experimental evidence does not distinguish between the possibilities. In ethylene the H-C-H angle¹³ is 117.37° but in tetramethylethylene the Me-C-Me angle¹⁴ is $110.5 \pm 2^\circ$.

¹²J.A. Pople, Quart. Revs., 11, 273 (1957).

¹³H.C. Allen and E.K. Plyler, J. Am. Chem. Soc., 80, 2673 (1958).

¹⁴L. Pauling and L.O. Brockway, J. Am. Chem. Soc., 59, 1223 (1937).

Mulliken¹⁵ has suggested a third possibility, that the two single bonds on each carbon atom (i.e. those not involved in formation of the double bond) may be described as $s^{1/4} p^{3/4}$, and the orbital involved in formation of the σ component of the double bond as $s^{1/2} p^{1/2}$. In this way there is still a total of one s electron and two p electrons, leaving the third p electron available for formation of the π component of the double bond. This model is then generally similar to the molecular orbital representation except that the 'external' valence angles would be tetrahedral. By supposing that cases intermediate between that just described and the sp^2 - π bond model can exist, one can account for the experimentally observed variation of angle in substituted ethylenes between approximately 110° and 120° . Dewar¹⁶, on the other hand, prefers to consider the possibility of non-linear overlap of orbitals.

Whatever model of the carbon-carbon double bond one chooses to adopt, there would seem to be no a priori reason why it should not be equally applicable to silicon. It is possible that the radius of the silicon 3p orbital is

¹⁵R.S. Mulliken, Tetrahedron, 6, 68 (1959).

¹⁶M.J.S. Dewar and H.N. Schmeising, Tetrahedron, 11, 96 (1960).

much greater than that of the carbon 2p orbital so that overlap is not possible, but the same argument would not apply to a silicon-silicon double bond. Nevertheless, evidence for such bonds is even scantier than for carbon-silicon double bonds.

Early Attempts to Prepare Carbon-Silicon
Double Bonds and Their Analogues

An excellent review of the chemistry of silicon up to 1947 has been given by Burkhard, Rochow, Booth, and Hartt¹⁷.

Gilman¹⁸ reports that in an early paper Kipping claimed to have prepared $(C_6H_5)(C_2H_5)Si:Si(C_2H_5)(C_6H_5)$ but did not refer to it again. Certainly in 1927 Kipping² stated his belief that an ethylenic binding between silicon and carbon cannot be formed or can, at best, be produced only under exceptional conditions.

In 1912 Schlenk and Renning¹⁹ claimed that on prolonged distillation of diphenylmethylsilanol, water was

¹⁷C.A. Burkhard, E.G. Rochow, H.S. Booth, and J. Hartt, Chem. Revs., 41, 97 (1947).

¹⁸H. Gilman and G.E. Dunn, J. Polymer Sci., 9, 253 (1953).

²F.S. Kipping, op. cit.

¹⁹W. Schlenk and J. Renning, Ann., 394, 221 (1912).

lost and a compound whose analysis corresponded to $(C_6H_5)_2Si:CH_2$ was obtained. The compound did not exhibit the behaviour expected from this formula since it did not add bromine. Kipping² repeated this work and found that water was indeed lost on heating but he was unable to find any evidence of unsaturation in the products. He pointed out that Schlenk and Renning¹⁹ had based their formula on only one analysis. Kipping was not able to prepare pure diphenylmethylsilanol but found that the product from prolonged distillation of the crude silanol could be separated by distillation under reduced pressure into two fractions, one boiling at 165-185°/45 mm and the other at 270°/45 mm. The lower boiling fraction did not decolourise bromine in chloroform nor react with aqueous potassium permanganate. The higher boiling fraction was a thick yellow oil readily soluble in ether, petroleum ether, acetone and other common solvents but only sparingly soluble in cold alcohol. This was identified as 'diphenylmethylsilicyl oxide', for which the current name is syn tetraphenyldimethyldisiloxane. Kipping concluded that Schlenk and Renning's product was a mixture.

²F.S. Kipping, op. cit.

¹⁹W. Schlenk and J. Renning, op. cit.

Since then Kipping's conclusion has been fully substantiated. It is now well-established that on prolonged heating of a silanol condensation products are formed, disiloxanes from a monosilanol and polysiloxanes from diols and triols.

Kipping attempted unsuccessfully to prepare compounds containing a carbon-silicon double bond using conventional methods of dehydration and dehydrohalogenation. He found that reaction of tribenzylchlorosilane with quinoline or dimethylaniline did not yield unsaturated products, though Kipping did not state what compounds were formed. Tribenzylsilanol did not react at all with acetic anhydride, phosphorus pentoxide, or zinc chloride. On distillation of compounds containing a chlorosilane group next to a methylene group, hydrogen chloride was not lost.

Kipping and Sands²⁰ found that the action of sodium on diphenyldichlorosilane gave a complex mixture from which three halogen free fractions were obtained. One of these had the formula $\text{Si}_4(\text{C}_6\text{H}_5)_8$ (compound A). It reacted with iodine to form a compound of formula $\text{Si}_4(\text{C}_6\text{H}_5)_8\text{I}_2$, which reformed compound A with sodium in boiling xylene, and with water

²⁰F.S. Kipping and J.E. Sands, J. Chem. Soc., (1921) 830.

formed a compound of formula $\text{Si}_4(\text{C}_6\text{H}_5)_8\text{O}$. Compound A also reacted with boiling tetrachloroethane to form a compound of formula $\text{Si}_4(\text{C}_6\text{H}_5)_8\text{Cl}_2$, which also reacted with water to form another compound of the formula $\text{Si}_4(\text{C}_6\text{H}_5)_8\text{O}$. With nitrobenzene, compound A formed another compound of formula $\text{Si}_4(\text{C}_6\text{H}_5)_8\text{O}_2$. The molecular weight of compound A, determined ebullioscopically in benzene, was about 700 [$\text{Si}_4(\text{C}_6\text{H}_5)_8$ requires 748].

Another fraction (compound B) was also found by Kipping and Sands to have the formula $\text{Si}_4(\text{C}_6\text{H}_5)_8$ and to react with bromine but not with iodine.

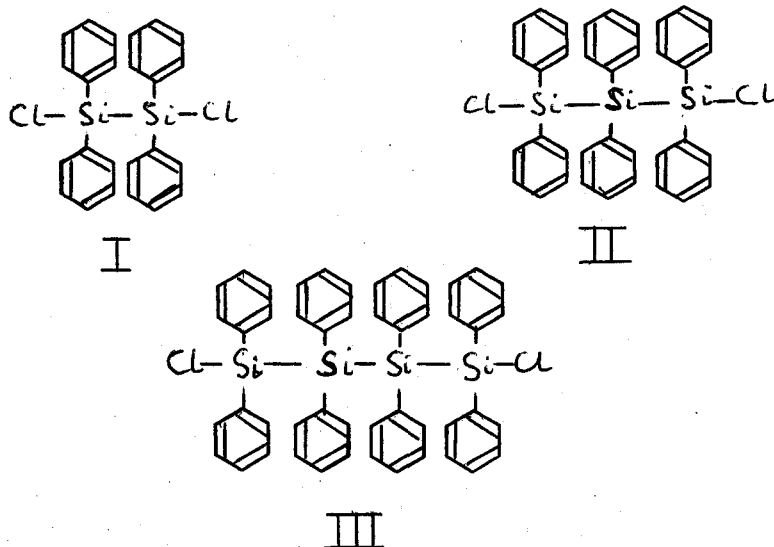
In an extension of this work Kipping, Murray and Maltby²¹ found that the action of sodium on phenyltrichlorosilane gave a complex mixture.

Kipping, having already come to the conclusion that doubly bonded silicon could not exist, formulated compound B or 'saturated octaphenyltetrasilane' as a saturated compound with a cyclotetrasilane ring and the compound A as possibly involving a saturated tetrahedron of silicon atoms or, in accordance with its description as 'unsaturated octaphenyltetrasilane', as an open chain compound containing a chain

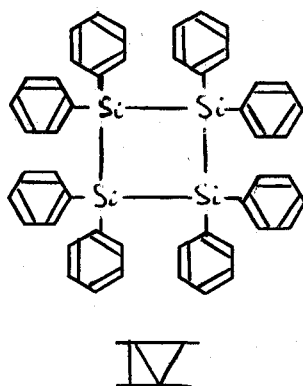
²¹F.S. Kipping, A.G. Murray and J.G. Maltby, J. Chem. Soc., (1929) 1180.

of four silicon atoms with the two end atoms tervalent, the free valencies being available for addition of halogens.

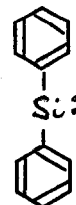
Although reasonable in its chronological setting, the above ideas are improbable in terms of modern ideas of valency. It is now known that the reaction is a coupling reaction very similar to the Wurtz and that compounds are formed of the types exemplified by I, II and III of which



the last could cyclise to compound IV or a carbene-like



intermediate (V) might be formed. It could then couple and dimerise to give compound IV. Gilman and co-workers²² have recently reinvestigated this reaction and have shown that the major product is indeed octaphenyl-tetracyclosilane. Kipping's method of reaction with sodium in boiling xylene could be used, or better, lithium in tetrahydrofuran. The product showed no free-radical character in its electron paramagnetic resonance spectrum and the 'addition' reactions were shown to be due to opening of the ring, presumably strained like its cyclobutane analogue.



It is indicative of the difficulties encountered in this work that the 'saturated octaphenyltetrasilane' or compound B formulated as $\text{Si}_4(\text{C}_6\text{H}_5)_8$ by Kipping on the basis of its molecular weight determined cryoscopically was later believed by Gilman²³ to have the composition $\text{Si}_6(\text{C}_6\text{H}_5)_{12}$, very recently amended²⁴ to $\text{Si}_5(\text{C}_6\text{H}_5)_{10}$, in both cases also on the basis of cryoscopically determined molecular weights.

²²A.W.P. Jarvie, H.J.S. Winkler, D.J. Peterson, and H. Gilman, J. Am. Chem. Soc., **83**, 1921 (1961).

²³A.W.P. Jarvie, *idem.*, *ibid.*, **83**, 4089 (1961).

²⁴H. Gilman and G.L. Schwebke, J. Am. Chem. Soc., **85**, 1016 (1963).

Milligan and Kraus²⁵ claimed to have prepared a compound which might be $[(C_6H_5)_3Ge]_2Si:Si[Ge(C_6H_5)]_2$ but do not appear to have referred to it again.

Di(-t-butyl)-silanediol does not condense to form a siloxane, presumably for steric reasons, but attempts to bring about intramolecular dehydration with formation of the silicon analogue of di(t-butyl) ketone were unsuccessful²⁶.

A report of 'Me₄Si₂' in a Japanese patent and its abstract in 'Chemical Abstracts'²⁷ proves to have been a misprint for Me₄Si²⁸.

Urry²⁹ reported that passage of silicon tetrachloride over 50% ferrosilicon at 600-1000° gave a compound of formula Si₆Cl₆, only slowly hydrolysed by water. The compound was described as a white crystalline solid of melting point 187°, soluble with no apparent change in methanol, chloroform, and ether, though an etherate could also be formed. With

²⁵J.S. Milligan and A. Kraus, J. Am. Chem. Soc., **72**, 5297 (1950).

²⁶L.H. Sommer and L.J. Tyler, J. Am. Chem. Soc., **76**, 1030 (1954).

²⁷Yo Shi-ihara, Jun Iyoda and Dai Takakashi, Japanese Patent 14617 (1961) - cf. Chem. Abs., **56**, 10190 (1962).

²⁸Yo Shi-ihara. Private communication to Dr. H. Kachi.

²⁹G. Urry, Abstracts of 133rd American Chemical Society Meeting, San Francisco, April 1958.

dimethylmercury at 25° a solid of melting point 73.2° with vapour density corresponding to the formula $\text{Si}_6(\text{CH}_3)_6$ was formed. This material showed absorption in the ultraviolet at $2600\text{--}2900 \text{ \AA}$ (hexamethylbenzene shows absorption at 2720 \AA). An ethereal solution of the material of formula Si_6Cl_6 and lithium borohydride gave a liquid of freezing point just below 0° , thought to have the formula Si_6H_6 . Urry at that time considered it possible that these materials were the first examples of silicon compounds analogous to benzene but now appears to have reached a different conclusion, though details are still lacking³⁰.

The Work of Fritz and Grobe

During the course of the present work Fritz and Grobe³¹ announced that pyrolysis of tetramethylsilane gave a mixture containing, among volatile products, the known compounds dimethylsilyltrimethylsilylmethane ($\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{H}$) and di-(trimethylsilyl)-methane ($\text{Me}_3\text{SiCH}_2\text{SiMe}_3$), and a new compound of formula $\text{Si}_2\text{C}_6\text{H}_{16}$. The products were partially

³⁰C. Eaborn, "Organosilicon Compounds", Butterworth, London (1960), p. 113.

³¹G. Fritz and J. Grobe, Z. anorg. u. allgem. Chem., **311**, 325 (1961).

separated by distillation, then purified by gas chromatography. Besides the two known compounds the third compound was isolated b.p. $122.8^{\circ}/745$ mm, $n_D^{20.3}$ 1.4430. Analysis (mean of several values) showed a composition of Si, 38.9%; C, 50.2%; H, 11.4%. Cryoscopic determination of the molecular weight in benzene gave a value of 135. The mass spectrum gave a value of 144. Hence Fritz and Grobe concluded that the compound had the formula $\text{Si}_2\text{C}_6\text{H}_{16}$, which requires Si, 38.9%; C, 50.0%; H, 11.1%; molecular weight 144.

The authors formulated the structure of the compound as $\text{Me}_2\text{Si}:\text{CHSiMe}_3$ on the grounds listed below.

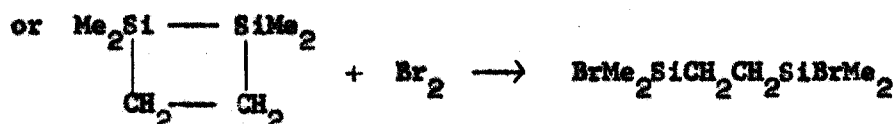
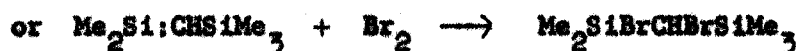
(a) Reaction of a mixture of the compounds $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$ and $\text{Si}_2\text{C}_6\text{H}_{16}$ with hydrogen bromide gave a compound with analysis corresponding to $\text{Me}_2\text{BrSiCH}_2\text{SiMe}_3$ ($\text{Me}_2\text{BrSiCHBrSiMe}_3$ as given in the original paper for reaction of the mixture with hydrogen bromide appears to be a misprint). The compound $\text{Si}_2\text{C}_6\text{H}_{16}$ was then isolated by gas chromatography. When dry hydrogen bromide was passed into the ice-cold material the same bromocompound, $\text{Si}_2\text{C}_6\text{H}_{17}\text{Br}$, was obtained in almost quantitative yield. The material was isolated by distillation. Since a carbon to silicon bond is polarised in the direction Si^+C^- , the addition of hydrogen bromide will lead to the formation of a compound with bromine attached to

the silicon atom. Hence it should be readily hydrolysed. In fact, the material was very readily hydrolysed by aqueous alcohol and it was even possible to estimate the bromine titrimetrically.

(b) Bromination of a mixture of $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$ and $\text{Si}_2\text{C}_6\text{H}_{16}$ gave again the compound $\text{Si}_2\text{C}_6\text{H}_{17}\text{Br}$. The authors attributed this to the bromination first of the silane hydrogen only of $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$, forming $\text{Me}_2\text{BrSiCH}_2\text{SiMe}_3$ and hydrogen bromide. The latter then added to $\text{Si}_2\text{C}_6\text{H}_{16}$ to form more of the same bromide. Some $\text{Me}_2\text{SiBrCHBrSiMe}_3$ was also formed by dibromination of $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$, though it is not clear why bromine should not add to the 'unsaturated' material if it had the formula attributed to it.

For a mixture shown by gas chromatographic analysis to contain about two-thirds saturated component, about one mole reacted with half a mole of bromine, as judged by the permanent red colour on addition of more bromine.

The expected reactions would be:



and in each case one mole of compound would react with one mole of bromine.

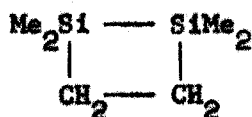
The purified monobromoproduct was treated with methyl magnesium iodide, forming a 165% yield (based on $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$) of di-(trimethylsilyl)-methane $[(\text{Me}_3\text{Si})_2\text{CH}_2]$.

The compound $\text{Si}_2\text{C}_6\text{H}_{16}$ reduced silver ion in acidic solution and did not evolve hydrogen with alkali; this point indicated the absence of SiH groups. In the infrared spectrum there was only a very weak band at 1050 cm^{-1} , whereas the compounds $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$ and $(\text{Me}_3\text{Si})_2\text{CH}_2$ showed a strong band there. This was assigned to the Si-CH₂-Si group. The authors believed that this distinguished the compound from $\text{H}_2\text{C}:\text{SiCH}_2\text{SiMe}_3$, which would give the same bromo-compound.

The authors pointed out that in both the carbon and the silicon series the relative abundance of peaks corresponding to fragments of high molecular weight increases as double bonds are introduced into the molecule³². Similarly fragments of molecular weight 144 appeared to the extent of 0.05% in the case of $\text{Me}_3\text{SiCH}_2\text{SiMe}_3$, 0.55% in the case of $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$, and the unusually high figure of 20.2% in the case of $\text{Si}_2\text{C}_6\text{H}_{16}$. The refractive index was unusually high; values found for $(\text{Me}_3\text{Si})_2\text{CH}_2$, $n_D^{19.3} = 1.4191$, for $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$, $n_D^{20.2} = 1.4170$, while for $\text{Si}_2\text{C}_6\text{H}_{16}$, $n_D^{20.3} = 1.4430$.

³²G. Fritz and J. Grobe, Z. anorg. u. allgem. Chem., **309**, 77 (1961).

Another possibility considered by the authors is that the reducing properties could be due to the presence of a silicon-silicon linkage, presumably of the structure VI.



VI

This was rejected on the grounds that bromination of such a compound should give a dibromide and that the compound is improbable on steric grounds. However it seems equally likely to the present author that the suggested mechanism of formation of hydrogen bromide and reaction of the latter with $\text{Si}_2\text{C}_6\text{H}_{16}$ would be equally probable. Also, since 1,1,2,2-tetramethyl-3,4-dimethylenecyclobutane is known³³, there appears to be no good reason why the structure shown could not exist. More convincing evidence is that the dibromocompound obtained had only one readily hydrolysable bromine atom, and hence was assigned a structure with one SiBr and one CBr group.

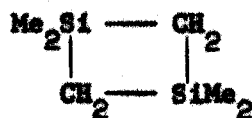
The above evidence is by no means conclusive. If the analogy between carbon-carbon double bonds and silicon-carbon double bonds is so close that the latter will add hydrogen bromide, one would also expect it to add bromine

³³E.N. Gapon, *J. Gen. Chem. U.S.S.R.*, 1, 496 (1931)
- cf. *Chem. Abs.*, 26, 4580 (1932).

and form $\text{Me}_2\text{SiBrCHBrSiMe}_3$ as a major product. The latter compound however was reported as a minor product, attributed to reaction of $\text{Me}_2\text{HSiCH}_2\text{SiMe}_3$ with bromine. However, the present author's experience has been that such vicinal silicon-carbon dibromides are extremely labile. One might, however, postulate that on account of the different electronegativities of silicon and bromine the π electrons of the double bond are so polarised that an intermediate bromonium ion could not be formed.

It is very surprising that the authors quoted on evidence of a band in the infrared spectrum attributable to a silicon-carbon double bond. In unsymmetrical olefines the ethylenic stretching frequency is usually quite intense and bands involving silicon are usually intensified relative to their carbon analogues.

It is therefore probable that the compound formed was actually 1,1,3,3-tetramethyl-1,3-disilacyclobutane (VII),



VII

which has been described³⁴ as a liquid b.p. 117-119°, n_D^{27} 1.4380.

³⁴W.H. Knoth, Jr. and R.V. Lindsey, Jr., J. Org. Chem., 23, 1392 (1958).

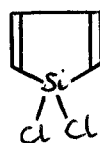
It reacts with silver nitrate to form a silver mirror and decolourises bromine water.

[Since the above was written, Frits, Grobe and collaborators^{35a} have concluded, after comparison of proton magnetic resonance, infrared and Raman spectra, as well as chemical properties, that their compound $\text{Si}_2\text{C}_6\text{H}_{16}$ was indeed 1,1,3,3-tetramethyl-1,3-disilacyclobutane, in agreement with the authors of another very recent paper^{35b}.]

The Work of Benkeser

In some recent papers Benkeser and co-workers³⁶ have reported what they describe as the first example of a silicoaromatic compound.

1,1-Dichlorosila-2,4-cyclopentadiene (VIII) was



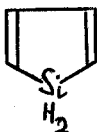
VIII

^{35a} G. Frits, W. Kemmerling, G. Sonntag, H.J. Becker, E.A.V. Ebsworth, and J. Grobe, Z. anorg. u. allgem. Chem., **321**, 10 (1963).

^{35b} R. Mueller, R. Koehne, and H. Bayer, Ber. **95**, 3030 (1962).

³⁶ R.A. Benkeser, R.F. Grossman, and G.M. Stanton, J. Am. Chem. Soc., **83**, 5029 (1961); ibid., **84**, 4723, 4727 (1962).

reduced by lithium aluminium hydride in dimethylcarbitol to sila-2,4-cyclopentadiene (IX). The latter compound was found



IX

to have the following physical properties: b.p. 60-62°, n_D^{25} 1.4265, $\lambda_{\max}^{\text{ether}}$ 232 μ , $\log \epsilon_{\max}$ 3.8. For comparison, cyclopentadiene has b.p. 42.5°, n_D^{19} 1.4446, $\lambda_{\max}^{\text{hexane}}$ 238.5 μ , $\log \epsilon_{\max}$ 3.53. The properties of sila-2,4-cyclopentadiene therefore appear to be quite comparable with those of its carbon analogue.

When sila-2,4-cyclopentadiene was treated with potassium sand in tetrahydrofuran or benzene or octane, the ion X, analogous to the cyclopentadienide ion, was reported



X

to be formed.

The ultraviolet spectrum of the silacyclopentadienide ion and that of potassium cyclopentadienide were reported to be very similar.

Nuclear magnetic resonance spectra were also in accord with the proposed formulas. 1,1-Dichlorosila-2,4-cyclopentadiene (VIII) showed doublet CH peaks, ratio of areas 1:1 at 2.48 τ . Sila-2,4-cyclopentadiene (IX) showed doublet CH peaks at 2.96 τ and an SiH peak at 4.12 τ (areas in the ratio 1:1:1). The silacyclopentadienide ion (X) in tetrahydrofuran had CH peaks at 2.70 τ and 2.90 τ , SiH at 3.95 τ (areas in the ratio 1:1:0.5), arising from two α hydrogen atoms, two β hydrogen atoms and one hydrogen atom bonded to silicon.

The silacyclopentadienide ion reacted with bromobenzene to form 1-phenyl- and 1,1-diphenyl- sila-2,4-cyclopentadiene.

It is significant that the open chain analogue of sila-2,4-cyclopentadiene, viz. divinylsilane (XI) did not



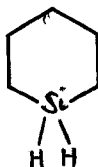
XI

react with potassium sand, suggesting that the resonance stabilisation of a closed π electron system is required for formation of the ion.

It would be strong evidence for the ability of silicon to form double bonds if the above work could be confirmed. However, in a recent very brief note³⁷, the authors have reported that they have not been able to reproduce the work and have withdrawn their claims pending further investigation.

Other Work

West³⁸ was unable to dehydrogenate silacyclohexane (XII) over platinum or palladium at 500°. Plate and Belikova³⁹



XII

tried to dehydrogenate the dimethyl derivative of the same compound but without success.

³⁷R.A. Benkeser and G.M. Stanton, J. Am. Chem. Soc., 85, 834 (1963).

³⁸R. West, J. Am. Chem. Soc., 76, 6012 (1954).

³⁹A.F. Plate and N.A. Belikova, J. Gen. Chem. U.S.S.R., 27, 2529 (1957) English translation.

CHAPTER II - THEORETICAL CONSIDERATIONS

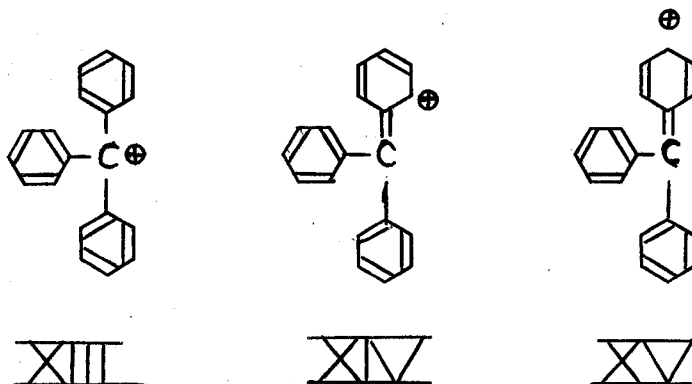
Evidence for the Participation of Silicon in Resonance Forms

In view of the lack of success in attempts to synthesise compounds which contain either a carbon-silicon or silicon-silicon double bond, there has been much interest in the ability of silicon to participate in resonance forms in which it may be represented as doubly bonded. In spite of a rather large number of investigations, there appears to be as yet little agreement.

Gilman and Dunn⁴⁰ have found the ultraviolet absorption spectrum of triphenylcarbinol to be generally similar to that of triphenylsilanol but the effect of added hydrochloric acid is quite different: in the case of triphenylcarbinol, addition of acid produces a bathochromic displacement of the wavelength of maximal absorption but no such effect is noted with triphenylsilanol. The difference is even more marked with the p-dimethylamino- derivatives.

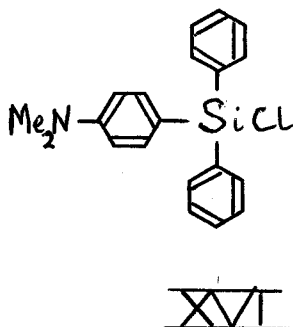
⁴⁰H. Gilman and G.E. Dunn, J. Am. Chem. Soc., 72, 2178 (1950).

In the case of the triphenylcarbinol and its derivatives, the spectrum measured is that of the ion $(C_6H_5)_3C^+$ for which ten resonance structures of the forms exemplified by XIII, XIV and XV may be written. In the case of triphenylsilanol

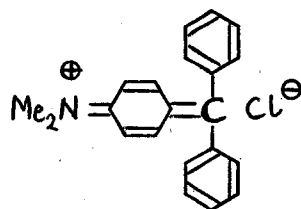


the absence of bathochromic wavelength displacement in the ultraviolet spectrum on addition of acid indicates that the ion $(C_6H_5)_3Si^+$, if formed, is not stabilised in the same way on account of the inability of the silicon atom to form double bonds.

A related piece of evidence from the same authors is that Hammett's ρ constant for the compound *p*-dimethylaminotriphenylchlorosilane (XVI) is different from that



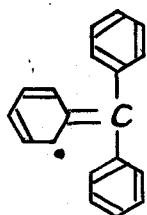
found in the corresponding substituted chlorotriphenylmethane. Since the σ constant is usually taken to be a measure of combined inductive and resonance effects and since the latter are represented formally as involving an increased proportion of canonical forms of the type exemplified by XVII, one



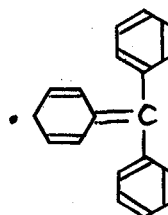
XVII

concludes that analogous interactions cannot take place in the silicon series.

Similarly the stability of the triphenylmethyl radical is attributed to the possibility of resonance among canonical forms of the type of Fig. XVIII, XIX, etc. On the



XVIII



XIX

other hand, triphenylchlorosilane does not give triphenylsilyl radicals with sodium, nor does hexaphenyldisilane dissociate as does hexaphenylethane. Indeed, tri-*o*-tolyl- and tri-*o*-naphthyl- chlorosilanes do not react with sodium at all, though the corresponding carbon compounds readily form free radicals.

As has been mentioned above, there is no evidence for the existence of silicon to oxygen double bonds similar to those found in carbonyl compounds^{41,42}, not even in silicates.

Kriegsmann and Beyer⁴³ have examined the infrared and Raman spectra of compounds of the following structures: $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$, $(\text{MeO})_3\text{SiC}\equiv\text{CSi}(\text{Me})_3$, and $\text{Cl}_3\text{SiC}\equiv\text{CSiCl}_3$. They concluded that there is free rotation about the silicon-carbon bond and hence no delocalisation of π electrons across these bonds.

In the compound trimethylsilylsulphide $[(\text{Me}_3\text{Si})_2\text{S}]$ both infrared and Raman spectra showed the bond order of the carbon-silicon bond to be 1.00 and in $(\text{Me}_3\text{Si})_2\text{CH}_2$ the force

⁴¹N. Wright and M.J. Hunter, J. Am. Chem. Soc., **69**, 803 (1947).

⁴²A.N. Lazarev, Zh. Obshch. Khim., **31**, 4061 (1961) - cf. Chem. Abs., **57**, 6629 (1962).

⁴³H. Kriegsmann and H. Beyer, Z. anorg. u. allgem. Chem., **311**, 180 (1961).

constants of the central silicon-carbon bonds are also consistent with a bond order of 1.00⁴⁴.

Other workers, on the other hand, have produced evidence that electrons can be delocalised across a silicon atom, or that silicon can take part in resonance forms in which it is represented as doubly bonded.

Motonori Kanazashi⁴⁵ found that the compound ClHC:CHCMe₃ eliminates hydrogen chloride with dilute alkali, but the compound ClHC:CHSiMe₃ does not. He attributed this to the participation of resonance forms of the type Cl[⊕]:CH.CH:Si[⊖]. This would therefore require not only the ability of silicon to form double bonds but also its ability to be pentacovalent, i.e. its ability to use its d orbitals in bonding.

Trisilylamine, (H₃Si)₃N, would be expected to be a good electron donor since the electronegativity of silicon is less than that of nitrogen. Hence the lone pair of electrons on nitrogen should be readily available for bonding. However, in fact, the compound forms only a very unstable complex with boron trifluoride⁴⁶ and is therefore a

⁴⁴H. Kriegsmann, Z. Electrochem., 61, 1088 (1957).

⁴⁵Motonori Kanazashi, Bull. Chem. Soc. Japan, 28, 44 (1955) - cf. Chem. Abs., 52, 4556 (1958).

⁴⁶A.B. Burg and E.S. Kuljan, J. Am. Chem. Soc., 72, 3103 (1950).

weaker base than trimethylamine. The original authors attributed this to the participation of the lone pair of electrons on nitrogen in double bonds of structures of the type $\text{H}_3\text{Si}^\ominus:\text{N}^\oplus(\text{SiH}_3)_2$. This type of bonding, if it exists, would also account for the fact that trisilylamine is planar⁴⁷ whereas trimethylamine is tetrahedral or pyramidal.

Nuclear magnetic resonance studies⁴⁸ have shown that in trimethylsilanol the hydroxylic proton is more protonic than that in trimethylcarbinol. This has been attributed to d-orbital resonance which would involve forms such as $\text{Me}_3\text{Si}^\ominus=\overset{\oplus}{\text{O}}\text{H}$. Other authors⁴⁹ have suggested that this involves one of the filled p orbitals of oxygen, the other filled p orbital being involved in disiloxanes. On the other hand it has been pointed out above that infrared evidence has shown no sign of double bond character in silicates⁴².

⁴⁷K. Hedberg, J. Am. Chem. Soc., 77, 6491 (1955).

⁴⁸L. Allred, E.G. Rochow and F.G.A. Stone, J. Inorg. and Nuclear Chem., 2, 416 (1956).

⁴⁹R.H. Baney, K.J. Lake, R. West and L.S. Whatley, Chem. and Ind., (1959) 1129.

⁴²A.N. Lazarev, op. cit.

Steward and Pierce⁵⁰ have shown that in silanes with unsaturated or aromatic substituents the acid catalysed hydrolysis of the Si-H bond is slower than in silanes with saturated substituents. They attributed this behaviour to dative π bonding to silicon.

Mironov and Chumsevskii⁵¹ have shown that in compounds of the formula $\text{Cl}_n \text{Me}_{3-n} \text{SiCH}:\text{CH}_2$ the ethylenic stretching frequency near 1600 cm^{-1} becomes stronger as n increases, the reverse is true for the band (at 1635 cm^{-1}) in compounds of the formula $\text{Cl}_n \text{Me}_{3-n} \text{SiCH}_2\text{CH}:\text{CH}_2$.

West and Kraihanzel⁵² compared the acetylenic stretching frequencies, CH stretching frequencies, basicities towards phenol and acidities towards dimethylformamide of compounds of formulae $\text{HC}\equiv\text{CSiMe}_3$ and $\text{HC}\equiv\text{CSi}(\text{C}_6\text{H}_5)_3$, with those of the corresponding 1-alkynes. They concluded that there is dative bonding from carbon to silicon in the former compounds.

⁵⁰O.W. Steward and O.R. Pierce, J. Am. Chem. Soc., **83**, 4932 (1961).

⁵¹V.F. Mironov and N.A. Chumsevskii, Doklady Akad. Nauk SSSR, **146**, 1117 (1962) - cf. Chem. Abs., **58**, 2024 (1963).

⁵²R. West and C.S. Kraihanzel, Inorg. Chem., **1**, 967 (1962).

Hague and Prince⁵³ have studied the ultraviolet absorption spectra (in cyclohexane) of a series of compounds of the formula $(C_6H_5)_3MX$ where M is Si, Ge, Sn, or Pb, and X is C_6H_5- , $-OH$, $-F$, $-Cl$, $-Br$, or $-M(C_6H_5)_3$. In all except the case where $X = -M(C_6H_5)_3$ the B band (for nomenclature see ref. 54) in the 230-270 $m\mu$ region shows benzenoid fine structure, but when X is $-M(C_6H_5)_3$ an intense K band appears. In the case of hexaphenyldisilane, $(C_6H_5)_6Si_2$, the ultraviolet absorption spectrum shows a maximum at 246.5 $m\mu$, $\epsilon_{max} = 32,600$. This would appear to suggest that conjugation takes place across the silicon-silicon bond.

Silyl isothiocyanate is not tetrahedral as one would expect, but linear⁵⁵, possibly on account of participation of the resonance form $H_3\overset{\ominus}{Si} = N = C = S$. Again, the Si-O-Si bond angle in siloxanes^{56,57} is about 150° , rather than the expected tetrahedral angle or right angle.

⁵³D.N. Hague and R.H. Prince, Proc. Chem. Soc., (1962) 300.

⁵⁴W.F. Forbes and R. Shilton, in American Society for Testing Materials STP No. 269, Symposium on Spectroscopy (1959) p. 176.

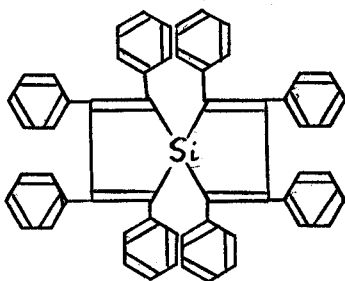
⁵⁵A.G. MacDiarmid and A.G. Maddock, J. Inorg. and Nuclear Chem., 1, 411 (1955).

⁵⁶R.F. Curi and K.S. Pitzer, J. Am. Chem. Soc., 80, 2371 (1958).

⁵⁷D.C. McKean, Spectrochimica Acta, 13, 38 (1958).

Some interesting work⁵⁸ shows that silicon in the β position to an aromatic ring shows unusual reactivity compared with that in the α or γ position. Thus, in the ultraviolet spectrum there is enhanced bathochromic displacement and the infrared spectrum shows an increased Si-C band intensity. The probable explanation is that the aromatic π electrons overlap the outer orbitals of the silicon atom in the β position.

The compound XX has been claimed⁵⁹ to show no

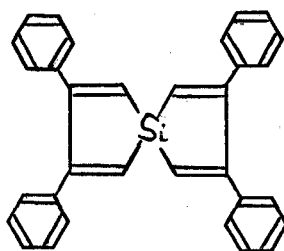


XX

aromatic character. However, the ion derived from bis(2,2'-biphenylene) silicon (XXI) by gain of two electrons

⁵⁸Yu.P. Egorov, L.A. Leites, N.G. Tolstikova, and E.A. Chernyshev, Izvest. Akad. Nauk SSSR. Otdel. Khim. Nauk, (1961) 410 (English translation).

⁵⁹E.H. Braye, W. Huebel and I. Caplier, J. Am. Chem. Soc., 83, 4406 (1961).



XXI

shows in its electron paramagnetic resonance spectrum behaviour that which would be expected of a system of 26 electrons delocalised across the silicon atom⁶⁰. However, the original authors point out that this can happen only because the two ring systems can be at right angles without loss of conjugation energy - a case without parallel in the carbon series.

Other evidence comes from inductive effects. Since silicon is more electropositive than carbon one would expect simple chlorosilanes to have a greater dipole moment than the corresponding carbon compound, but the reverse is found to be true, as shown in Table I.

⁶⁰R.D. Cowell, G. Urry and S.I. Weissman, J. Am. Chem. Soc., 85, 822 (1963).

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TABLE I⁶¹DIPOLE MOMENTS (DEBYE UNITS) OF CHLOROSILANES
AND CHLOROMETHANES

Si Compound	Dipole Moment	C Compound	Dipole Moment
SiH ₃ Cl	1.28	CH ₃ Cl	1.87
SiH ₂ Cl ₂	1.17	CH ₂ Cl ₂	1.56
SiHCl ₃	0.85	CHCl ₃	1.00

Contributions from the resonance form $\overset{\ominus}{\text{H}}_3\overset{\oplus}{\text{Si}}=\overset{\ominus}{\text{Cl}}$ could account for this difference. Also the importance of such structures as measured by their effect on dipole moment decreases in the order SiF > SiCl > SiBr^{62,63}, in accordance with the fact (unexplained but accepted) that elements of low period in the Periodic Table form double bonds more readily than those of higher period.

The dipole moments of a series of para-substituted phenyltrimethylsilanes (p-XC₆H₄SiMe₃) have been measured⁶⁴

⁶¹L.O. Brockway and I.E. Coop, Trans. Faraday Soc., 34, 1429 (1938).

⁶²C. Curran, R.M. Witucki, and P.A. McCusker, J. Am. Chem. Soc., 72, 4471 (1950).

⁶³E.L. Reilley, C. Curran, and P.A. McCusker, J. Am. Chem. Soc., 76, 3311 (1954).

⁶⁴H. Soffer and T. De Vries, J. Am. Chem. Soc., 73, 5817 (1951).

and the moment of the trimethylsilyl group calculated, assuming that the moment of the X group is the same as its value in other aromatic compounds. The moment which is attributed to the group $\text{Me}_3\text{Si}-$ varies considerably, indicating the possibility of contributions from resonance forms which in turn will depend on the ability of X to conjugate with the ring. Values are set out in Table II.

TABLE II
MOMENT OF Me_3Si GROUP IN $p\text{-XC}_6\text{H}_4\text{SiMe}_3$

X	H	NO_2	COOH	Br	Cl	F	Me	NH_2	NMe_2
Moment	+0.44	0.49	0.46	0.27	0.13	0.25	-0.06	-0.13	-0.26

Even in phenyltrimethylsilane itself the moment is 0.42 D, whereas that of *t*-butylbenzene is 0.53 D⁶⁵ although one would expect the silicon compound to have the higher dipole moment on account of the more electropositive character of silicon compared with carbon.

Siliconium Ions

The stability of many ions in the carbon series is usually attributed to the possibility of resonance among

⁶⁵H. Frieser, M.V. Eagle, and J. Speier, J. Am. Chem. Soc., 75, 2821 (1953).

several structures (cf. discussion of Gilman and Dunn's results⁴⁰ above). Effectively this spreads the positive charge over more atoms. So far there is no conclusive evidence for the existence of siliconium ions even as unstable intermediates. The triphenylmethylhalides form conducting solutions in liquid sulphur dioxide, nitromethane, nitrobenzene, and dimethylformamide, but the corresponding triphenylsilyl compounds have no significant conductance under the same conditions⁶⁶. Even the compound tri-(p-dimethylaminophenyl)-chlorosilane $[(p-NMe_2C_6H_4)_3SiCl]$ is not ionised, although the carbon analogue (Crystal Violet) is readily ionised in solution. Rochow et al.⁶⁷ believed that they had evidence from conductance measurements for the existence of siliconium ions but later reinterpreted their results as arising from hydrolysis by traces of water⁶⁸.

There is at present no evidence of reactions among silicon compounds by a mechanism analogous to the well-known

⁴⁰H. Gilman and G.E. Dunn, op. cit.

⁶⁶A.B. Thomas and E.G. Rochow, J. Inorg. and Nuclear Chem., 4, 205 (1957).

⁶⁷K. Gingold, E.G. Rochow, D. Seyferth, A.C. Smith, and R. West, J. Am. Chem. Soc., 74, 6306 (1952).

⁶⁸A.B. Thomas and E.G. Rochow, J. Am. Chem. Soc., 79, 1843 (1957).

SN1 type in the carbon series. A mechanism involving penta-covalent silicon is found in its place. This can involve sp^3d hybrid orbitals⁶⁹, a process improbable in the carbon series on account of the higher energy of the orbitals to be used relative to those already involved in bonding.

Sommer⁷⁰ believes that siliconium ions are not formed only because energetically more favourable paths are available. Negative ions have been detected⁷¹ and ions of the type $(C_6H_5)_3Si^-$ are known⁷².

Current Theoretical Considerations

The evidence presented above for electron delocalisation involving silicon is not necessarily comparable with that presented for carbon compounds. In the latter series, formation of a double bond requires overlap of two p orbitals to form a π bond. In the case of a carbon-carbon double bond both would be 2p orbitals. In a carbon-silicon

⁶⁹C. Eaborn, "Organosilicon Compounds", Butterworth, London (1960), pp. 103-113.

⁷⁰L.H. Sommer and G.A. Baughman, J. Am. Chem. Soc., **83**, 3746 (1961).

⁷¹M.G. Townsend, J. Chem. Soc., (1962) 51.

⁷²H. Gilman, O.L. Marrs, W.J. Trepka, and J.W. Diehl, J. Org. Chem., **27**, 1260 (1962).

double bond that on carbon would be $2p$, that on silicon $3p$. It is at once evident that equivalent symmetry of two orbitals is not a sufficient guarantee that they will combine to form a π bond; they may have such dissimilar radii that they do not overlap effectively. However, a silicon-silicon double bond would not be subject to this limitation but evidence for such is virtually non-existent.

Reverting to the discussion of carbon-silicon double bonds, the evidence for electron delocalisation across silicon is not germane since delocalisation can involve the readily available d orbitals of silicon, with pentagonal symmetry, each d orbital having 2 nodal planes, in contrast to the one of a p orbital. Indeed such orbitals would combine double bond character with free rotation about such a bond, since a $d_{\pi}-p_{\pi}$ bond could be formed with each d orbital in turn, whereas $p_{\pi}-p_{\pi}$ bonds are well-known to be resistant to twisting on account of the loss of bond energy thereby (Ref. 69, p. 98).

This has some bearing on the theoretically best way of attempting to prepare a compound containing a carbon-silicon double bond. It has usually been assumed that such a bond, if capable of existence, would be preferentially

⁶⁹C. Eaborn, op. cit.

stabilised by conjugation with aromatic groups. (Compare the relative ease of dehydrohalogenation of α -phenyl- β -haloethanes with the rather difficult dehydrohalogenation of primary alkyl halides.) Consequently the few deliberate attempts to prepare carbon-silicon double bonds have usually been attempts to prepare compounds of a type analogous to styrene, stilbene, α -phenylstyrene, or triphenylethylene. It now appears that the energy of π bonding between the silicon d orbitals and the aromatic π orbitals may be so favourable that little, if any, extra energy would be gained by conjugation of the more common type. It has been suggested⁷³ that compounds such as $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{Si} = \text{CH}_2 \\ \diagup \\ \text{CH}_3 \end{array}$ might be easier to form since in this case polymerisation would result in loss of all conjugation energy, whereas with the aryl substituted compounds the loss of conjugation energy on polymerisation could be, at least partially, regained by d_{π} - p_{π} conjugation. The present work does not support this suggestion. (It should be pointed out that the original authors presented it merely as a less unlikely method.)

Pitzer⁷⁴ in a discussion has suggested that repulsion

⁷³I.R. Beattie and T. Gilson, Nature, 193, 1041 (1962).

⁷⁴K.S. Pitzer, J. Am. Chem. Soc., 70, 2140 (1948).

between electrons in a bond and those in the inner shells of neighbouring atoms causes the interatomic distance between neighbouring atoms to be relatively greater than expected from the increase of atomic radius alone. This in turn reduces overlap of p orbitals to the point where it is insufficient for any gain of energy by formation of a π bond. This effect will, of course, be greater for second period elements than for those of the first period. Mulliken⁷⁵ has criticised these views on theoretical grounds.

Like the practical evidence, the theoretical evidence for carbon-silicon double bonds appears to be inconclusive.

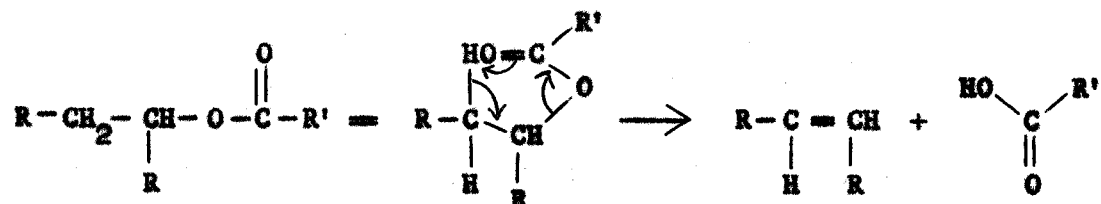
Preparation of Carbon-Carbon Double Bonds By Pyrolysis of Hydrogen Phthalates of Tertiary Alcohols

It has long been known that pyrolysis of esters (e.g. acetates and benzoates) over alumina or glass beads proceeds with elimination of an acid and formation of an olefine. This reaction, the Kraft's reaction, has been well-reviewed by De Puy⁷⁶. The mechanism may be represented as

⁷⁵R.S. Mulliken, J. Am. Chem. Soc., 72, 4493 (1950).

⁷⁶C.H. De Puy and R.W. King, Chem. Revs., 60, 431 (1960).

involving a cyclic transition state.

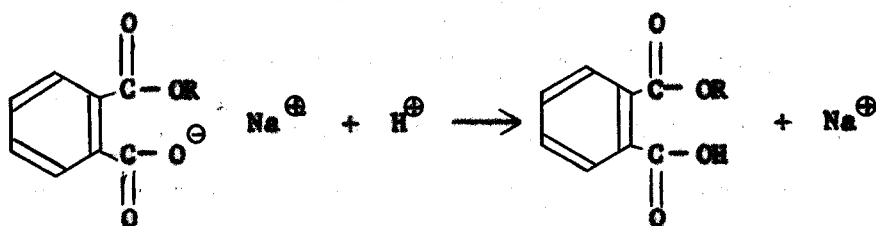
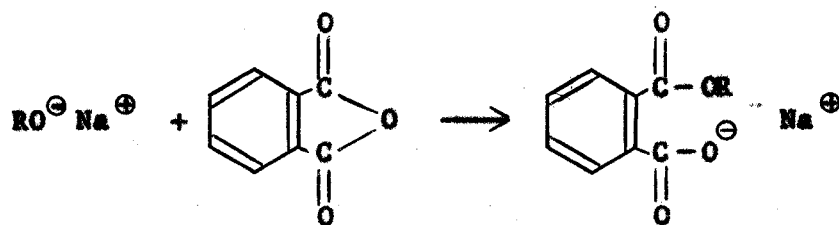
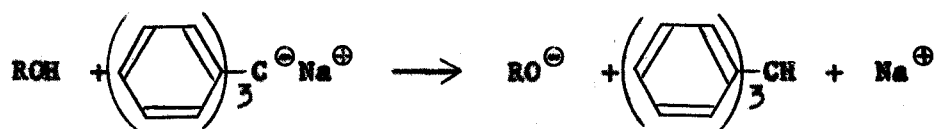


Tetrachlorophthalic acid has also been used as the acid component.

Work in this laboratory⁷⁷ has developed a novel method for preparation of the hydrogen phthalates of tertiary alcohols. Such esters are not readily accessible by conventional methods since the tertiary alcohol undergoes ready elimination of water to form an olefine under the usual esterification conditions. The method developed in this laboratory requires conversion of the alcohol to the alkoxide ion by titration with an ethereal solution of sodium triphenylmethyl. The end-point is readily detected by the persistence of the blood-red colour of the triphenylmethide ion. The solution of alkoxide ion is then stirred with phthalic anhydride whereupon the sodium salt of the hydrogen phthalate is formed. This is isolated by solution in water and then converted to the acid phthalate by pouring onto a mixture of crushed ice and hydrochloric acid. The reactions which occur are set out

⁷⁷K.G. Rutherford, J.M. Prokipcak and D.P.C. Fung, *J. Org. Chem.*, **28**, 582 (1963).

below.



The triphenylmethane formed is insoluble in water and hence readily separated. The hydrogen phthalate usually separates as a gum which is recrystallised from a chloroform-petroleum ether solvent pair. Yields are 30 to 85%.

It has also been found in this laboratory^{77,78} that the hydrogen phthalates of tertiary alcohols decompose at or near the melting point, usually below 150°, much lower than for acetates or benzoates. The reaction proceeds in reasonably good yield (50 to 60%) and appears to yield only olefine and

⁷⁷K.G. Rutherford, J.M. Prokipcak, and D.P.C. Fung, *J. Org. Chem.*, **28**, 582 (1963).

⁷⁸Idem. Private information.

phthalic acid, with a notable absence of tarring. Triphenyl-carbinyl hydrogen phthalate, in which there is no hydrogen atom in the position β to the phthalic acid does not decompose even at 300°C .

CHAPTER III - DISCUSSION OF EXPERIMENTAL RESULTS

Silyl Esters

It was hoped at the outset that the elimination of phthalic acid from hydrogen phthalate esters could be extended to the silicon series, since the mild conditions of the elimination might avoid polymerisation.

Although a reasonable number of silyl esters are known most are esters of inorganic acids. Indeed, in a list¹⁷ claimed to be complete up to the middle of 1946, only eight are given, namely di-(trimethylsilyl) sulphate, di-(triethylsilyl) sulphate, tri-(trimethylsilyl) phosphate, trimethylsilyl acetate, triethylsilyl acetate, ethyldiethoxysilyl acetate, tri-(n-propyl)-silyl acetate, and triphenylsilyl acetate.

Methods that have been used for preparing esters of silanols include:

- 1) Reaction of a chlorosilane with acetic anhydride⁷⁹.

¹⁷C.A. Burkhard, op. cit.

⁷⁹K.A. Andrianov, A.A. Zhdanov, and A.A. Bogdanova, Doklady Akad. Nauk SSSR, 94, 697 (1954) - cf. Chem. Abs., 49, 6087 (1955).

- ii) Reaction of a chlorosilane with the silver salt of an acid⁸⁰.
- iii) Reaction of a silanol with an acid chloride⁸¹.
- iv) Reaction of a chlorosilane with acid⁸².
- v) Reaction of a disiloxane with sulphuric acid⁸³.
- vi) Reaction of a disiloxane with an acid anhydride and zinc chloride⁸⁴.
- vii) Reaction of an alkoxysilane with an acid anhydride⁸⁵.
- viii) Reaction of a trialkylsilane with a carboxylic acid in presence of aluminium iodide and iodine⁸⁶.

⁸⁰C. Fape, Ber. Dtsch. Chem. Ges., 14, 1872 (1881).
See also H.H. Anderson and H. Fischer, J. Org. Chem., 19, 1296 (1945).

⁸¹N.S. Nametkin, A.V. Topchiev, and F.F. Machus, Doklady Akad. Nauk SSSR, 87, 233 (1952) - cf. Chem. Abs., 47, 12281 (1953).

⁸²Y. Etienne, Compt. Rend., 235, 966 (1952).

⁸³W. Patnode and D.F. Wilcock, J. Am. Chem. Soc., 68, 358 (1946).

⁸⁴J. Valade, C.R. Acad. Sci. Paris, 246, 952 (1958).

⁸⁵H.W. Post and C.H. Hofrichter, J. Org. Chem., 5, 443 (1946).

⁸⁶B.N. Dolgov, N.P. Kharitonov, and M.G. Voronkhov, J. Gen. Chem. Moscow, 24, 861 (1954) - cf. Chem. Abs., 49, 8094 (1955).

- ix) Reaction of an organosilicon chloride with an alkali metal salt of the acid⁸⁷.
- x) Transesterification⁸⁸.

Di- and tri- acetates have also been prepared⁸⁹ and found to react with diphenyldichlorosilane to give cyclic polysiloxanes.

No phthalates of organosilanols have been reported and the only attempt to prepare such appears to have been that of Gilman and Smart⁹⁰, who were unable to isolate any ester from the reaction of triphenylsilanol with phthalic anhydride.

Present Attempts to Prepare Silyl Hydrogen Phthalates and Pyrolysis Thereof

It appeared that for the present work the readily available compounds diphenylmethylchlorosilane and trimethylchlorosilane would be the most suitable, since the expected

⁸⁷H.A. Schuyten, J.W. Weaver, and J.D. Reid, J. Am. Chem. Soc., 69, 2110 (1947).

⁸⁸H.H. Anderson and G.M. Stanislow, J. Org. Chem., 18, 1716 (1953).

⁸⁹Yasuaki Nakaido and Toshio Takiguchi, J. Org. Chem., 26, 4144 (1961).

⁹⁰H. Gilman and G.N.R. Smart, J. Org. Chem., 16, 424 (1951).

products would have the structure $(C_6H_5)_2Si:CH_2$ which is stabilised by conjugation or $(CH_3)_2Si:CH_2$ which is not affected by d orbital interaction. (See above.) Initially it was intended to prepare the silyl hydrogen phthalates by the reaction described above via the silanolate ion. Since it was known that the silanols would condense readily to form disiloxanes, the first attempts were directed at preparation of the silanols.

Hydrolysis of Chlorosilanes

Preliminary experiments showed that diphenylmethylchlorosilane could be readily hydrolysed with water. The course of reaction was easily followed since the chlorosilane is denser than water and the silanol less dense. Hydrolysis could also be carried out by the use of a sodium bicarbonate solution. The product was extracted with ether and on evaporation of solvent a white oil remained. This oil was soluble in ether or benzene but formed no precipitate with a solution of phthalic anhydride in the same solvents. On standing for a few days this oil deposited crystals, m.p. $37-49^{\circ}$, apparently sym-tetraphenyldimethyldisiloxane. A repetition on a larger scale using sodium bicarbonate gave a turbid oil which solidified on attempted distillation giving the same disiloxane.

It is known that hydrolysis of chlorosilanes in acidic or basic media readily leads to condensation products, though special techniques have been developed by which this can be avoided. However, it was decided to use one of the other methods⁸⁷ that have been used for the preparation of silyl esters. The original authors shook an ethereal solution of the chlorosilane with a slurry of the sodium salt of the acid, the latter present in 100% excess. The reaction was carried out in a flask fitted with an exit tube which terminated in a fritted glass disc so that after completion of the reaction the solution of the silyl ester could be removed by filtration directly.

In the present work the reactants were shaken overnight (10-20 hours) using usually potassium hydrogen phthalate (0.5 mole), chlorosilane (0.25 mole) and solvent (200-300 ml.). Ether, benzene or carbon tetrachloride was used as solvent. The latter two were preferred because of the insolubility of phthalic acid in these solvents. In all cases a waxy solid was deposited and the solution became yellow. The precipitated solids were invariably covered with a thick gum that could be removed only by prolonged extraction in a Soxhlet

⁸⁷H.A. Schuyten, J.W. Weaver, and J.D. Reid, op. cit.

extractor using carbon tetrachloride or benzene. These solids consisted of mixtures of unreacted potassium hydrogen phthalate, potassium chloride and phthalic acid. Filtration proved to be extremely slow. Usually twelve hours or more via a water aspirator through a medium grade porosity sintered glass funnel was required for total separation. The yield of potassium chloride and residual potassium hydrogen phthalate usually indicated reaction to the extent of 50-75%.

The filtrate, after removal of solvent under reduced pressure, still contained chlorosilane as shown by hydrolysis to a disiloxane and reaction of the aqueous layer with silver nitrate. The filtrate was found to react slowly with bromine in carbon tetrachloride, depositing phthalic acid (see below). It also decolourised alkaline potassium permanganate, though slowly. Unfortunately these observations could not be taken as evidence for the formation of a carbon-silicon double bond since tetraphenyldimethyldisiloxane also slowly decolourised bromine water (although not bromine in carbon tetrachloride) and diphenylmethylchlorosilane slowly decolourised bromine water or bromine in carbon tetrachloride and reacted vigorously with bromine in acetic acid.

On attempted distillation of the product only a very small amount of liquid was obtained which on standing in

the refrigerator solidified to tetraphenyldimethyldisiloxane.

The materials which might have been diphenylmethylsilyl hydrogen phthalate proved to be extremely difficult to characterize, not only because of their gummy, uncrystallizable nature but also because of their extreme tendency to hydrolyse readily (cf. ref. 91). On standing, phthalic acid was invariably deposited but no material having the properties expected of the structure $(C_6H_5)_2Si:CH_2$ was ever isolated. Again, the infrared spectrum did not indicate the presence of such a linkage.

In one experiment, distillation of the filtrate gave diphenylmethylsilanol, the physical constants of which were in agreement with those previously reported⁹². The analysis was in agreement with calculated values. This compound reacted very slowly with bromine in carbon tetrachloride or acetic acid, but the undistilled residue (a brown gum) readily reacted with both. The distillate showed both free and hydrogen bonded hydroxyl in its infrared spectrum at 2.65 and 2.87 - 3.1 μ in carbon tetrachloride. In the presence of

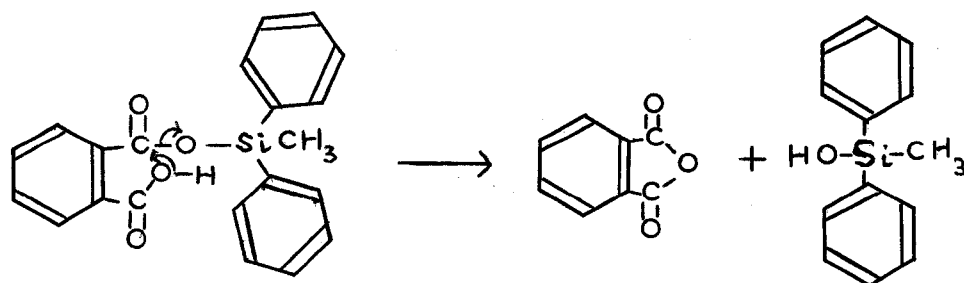
⁹¹D.N. Andreev and L.L. Shchukovskaya, Izvest. Akad. Nauk SSSR. Otdel. Khim. Nauk, (1953) 135 - cf. Chem. Abs., 48, 3244 (1954).

⁹²W.H. Daudt and J.F. Hyde, J. Am. Chem. Soc., 74, 386 (1952).

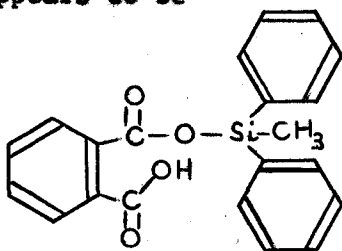
dilute hydrochloric acid it condensed to tetraphenyldimethyldisiloxane. During the distillation much trouble was experienced with a white solid which sublimed on the cooler areas of the apparatus. This was identified as phthalic anhydride.

In a separate experiment the crude diphenylmethylsilyl hydrogen phthalate was heated to reflux temperature for some hours. On cooling a precipitate was formed which was recovered by filtration and identified as phthalic anhydride. Distillation of the filtrate yielded diphenylmethylsilanol and more phthalic anhydride. Attempts at chromatographic separation yielded only impure diphenylmethylsilanol.

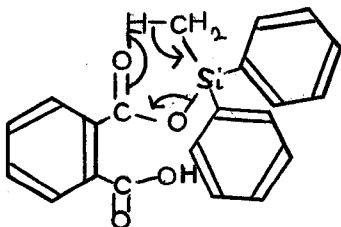
It is possible that the diphenylmethylsilanol formed was merely an artifact of hydrolysis of the initially formed ester. However the high yield of product makes this unlikely particularly when distillation was carried out soon after preparation of the ester. It is to be concluded that the mode of decomposition is that shown by the equation



Although not reported for tertiary alcohols the same reaction has been found to occur with primary and secondary alcohols^{93,94,94} such as cyclohexylmethyl hydrogen phthalate and sec-butyl hydrogen phthalate. The preferred transition state appears to be



though there seems to be no reason why the alternative transition state



leading to the compound $\text{CH}_2 = \text{Si}(\text{C}_6\text{H}_5)_2$ should not be used.

⁹³ G.P. Shulman, J.H. Bennett, and D.G. Botteron, J. Org. Chem., **27**, 3923 (1962).

⁹⁴ K.G. Rutherford and D.P.C. Fung. Private information.

⁹⁵ R.H. Lombaers, Bull. soc. chim. Belg., **33**, 232 (1924) - cf. Beilstein's Handbuch der Organischen Chemie, E II, vol. 9, p. 587.

Possibly the differing electronegativities of silicon and carbon make the methyl carbon so negative that the carbonyl oxygen is repelled. Also the incipient siliconium ion appears reluctant to form.

Silylidene diacetates are known⁹⁶ to decompose forming acetic anhydride and a polymeric siloxane. The expected silicon analogue of a ketone is not obtained although it presumably is an intermediate in the formation of the polymer.

Trimethylsilyl Hydrogen Phthalate

In view of the difficulty experienced with diphenylmethylsilyl hydrogen phthalate and in view of the theoretical prediction that $(\text{CH}_3)_2\text{Si}:\text{CH}_2$ might be more stable than a compound containing an aromatic ring conjugated with the double bond, an attempt was made to prepare trimethylsilyl hydrogen phthalate.

The same general method which was successful for the preparation of diphenylmethylsilyl hydrogen phthalate was used. Trimethylchlorosilane (0.25 mole) and potassium hydrogen phthalate (0.5 mole) were mechanically shaken for 15-20 hours with benzene (approximately 300 ml.).

⁹⁶ K.A. Andrianov, A.A. Zhdanov, and S.A. Pavlov, Doklady Akad. Nauk SSSR, **102**, 85 (1955) - cf. Chem. Abs., **50**, 4771 (1956).

Again the residue was a white solid which was shown by acetone extraction to contain phthalic acid. The filtrate was again yellow and was very readily hydrolysed. On one occasion a distillate was obtained from which phthalic acid was precipitated on the addition of bromine but analysis showed that silicon was present only in the amount of 1.47% (calculated for trimethylsilyl hydrogen phthalate, 11.8%). This hydrogen phthalate also reacted at once with bromine in acetic acid. Phthalic acid was deposited. In another run a distillate was obtained, b.p. 69-84° (literature values for trimethylsilanol and hexamethyldisiloxane are 100 and 100.5° respectively; Sauer³ reports that a mixture of the two boils at 88°). Considerable phthalic acid sublimed in the distillation apparatus and on filtration of the undistilled residue a further quantity of phthalic acid was obtained. The distillate continued to show a wide range of boiling point on further distillation and was found by qualitative tests to contain silicon but no halogen. Analysis showed the distillate to have the composition: C, 34.76%; H, 8.04%; Si, 12.79%. This corresponds to a formula $C_{6.35}H_{17.5}Si_{1.00}O_{6.1}$ and hence the nature of the distillate remains obscure.

³R.O. Sauer, op. cit.

Preparation of Silyl Benzoates

In view of the extreme practical difficulties experienced in working with the silyl hydrogen phthalates it was of interest to see whether the difficulties were due to the nature of the compounds or the methods used. With this end in mind it was decided to attempt the preparation of the corresponding silyl benzoates. The method used was essentially that used for the preparation of the hydrogen phthalates.

Diphenylmethylsilyl Benzoate

In a preliminary experiment a mixture of diphenylmethylchlorosilane (0.17 mole) and sodium benzoate (0.25 mole) was shaken with carbon tetrachloride (200 ml.) for nineteen hours. Again a white precipitate was formed which on filtration via water aspirator became a hard white mass. Distillation of the yellow filtrate (after removal of solvent in vacuo) yielded impure diphenylmethylsilyl benzoate, as indicated by the infrared spectrum.

In a similar experiment using this time one-quarter mole diphenylmethylchlorosilane and one-half mole sodium benzoate in benzene (400 ml.) the usual white precipitate was formed and this was extracted with benzene. This benzene extract was combined with the original filtrate. The solid residue was shown by analysis to contain 3.7% benzoic acid

and 22% sodium chloride, the latter corresponding to 89% of the theoretical yield. The extract and filtrate on evaporation yielded an oil which on titration with sodium hydroxide showed a rather high neutralisation equivalent of 370 (calculated for diphenylmethylsilyl benzoate, 318). On heating this oil darkened and on distillation in vacuo a small amount of benzoic acid sublimed on the cooler walls of the apparatus. Some small quantities of materials not further investigated were obtained along with a large fraction shown by elemental analysis and infrared spectroscopy to be diphenylmethylsilyl benzoate.

Trimethylsilyl Benzoate

This compound was prepared in 5% yield by shaking trimethylchlorosilane with an excess of sodium benzoate in carbon tetrachloride. Physical constants were in agreement with those reported in the literature.

Distillation of Silyl Benzoates

Both benzoates distilled in vacuo unchanged and though readily hydrolysed were not as labile to water as the hydrogen phthalates.

Conclusion

It appears that attempts to prepare silyl hydrogen phthalates might be successful if carried out entirely in a

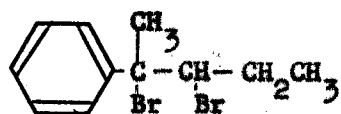
dry atmosphere. Pyrolysis would yield a silanol and phthalic anhydride. It might be possible to 'crack' the benzoates, but it is very unlikely that any compound containing a carbon-silicon double bond would be isolated. There is, however, a possibility that a polymer of such a compound might be obtained.

Reaction of Tertiary Hydrogen Phthalates
with Bromine

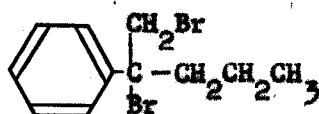
The most obvious test for the presence of a carbon-silicon double bond would be the addition of bromine. It was observed however that the silyl hydrogen phthalates themselves reacted readily with this reagent. The bromine was usually decolourised rapidly and a white precipitate was formed which was identified as phthalic acid. Preliminary experiments showed the silicon containing component to be extremely difficult to isolate so the reaction was investigated in the carbon series.

Phenylmethyl-n-propyl-carbinyl hydrogen phthalate was treated with an equimolar quantity of bromine in carbon tetrachloride. Overnight a white solid was deposited and on recrystallisation from water a yield of 82.5% of phthalic acid was obtained. The filtrate was washed to remove bromine and distilled whereupon two fractions were obtained, apparently

the same material in different states of purity. Analysis showed less bromine than calculated for the dibromides of structures XXII and XXIII. However, bromine is readily lost



XXII



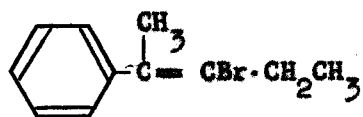
XXIII

from such vicinal dihalides. Zinc dust debromination of the remaining material gave a compound which reacted slowly with bromine in carbon tetrachloride and rapidly with bromine in acetic acid. This showed ultraviolet absorption at λ_{\max} 243 m μ , ϵ_{\max} 7,300. α -n-Propylstyrene absorbs maximally at 239 m μ , ϵ_{\max} 9,400⁹⁷ and α,β -dimethylstyrene at 244 m μ , ϵ_{\max} 8,700⁹⁸. Since α -methyl- β -ethylstyrene should show much the same absorption as the latter compound it is concluded that the debrominated product is probably about 80% pure α -methyl- β -ethylstyrene. Analysis supported this. Carbon and hydrogen figures did not total 100%. The difference was assumed to be bromine, corresponding to about 16% of a debromination product of structure

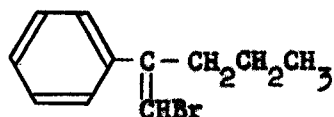
⁹⁷C.G. Overberger and D. Tanner, J. Am. Chem. Soc., 77, 369 (1955).

⁹⁸Y. Hirschberg, J. Am. Chem. Soc., 71, 3241 (1949).

XXIV or XXV. This material was not further investigated.



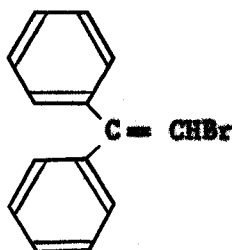
XXIV



XXV

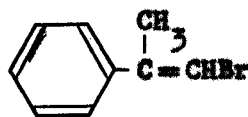
Similar treatment of *t*-butyl hydrogen phthalate yielded after several hours a small amount of phthalic acid. In the residue, after removal of solvent, there was a small amount of a dark-coloured liquid and the characteristic odour of a bromo-compound but not enough was obtained for further investigation.

The reaction was also investigated using diphenylmethylcarbonyl hydrogen phthalate. This material reacted completely with bromine in carbon tetrachloride over a period of 24 hours. Phthalic acid was removed by filtration and was obtained in 90% yield. The filtrate, a fuming liquid, liberated iodine from potassium iodide. After repeated washing with sodium hydroxide, bromine still appeared to be evolved as judged by the appearance of a reddish coloration. Solvent was removed by distillation and a black oil remained. Crystallization of this oil from ethanol yielded yellow crystals which were identified as α -phenyl- β -bromostyrene (XXVI),

XXVI

by melting point and elemental analysis. The structure was further elucidated by oxidation to benzophenone which was identified as its 2,4-dinitrophenylhydrazone derivative.

Dimethylphenylcarbinyll hydrogen phthalate reacted fairly rapidly with bromine in carbon tetrachloride, though not as rapidly as phenyldimethylcarbinyll hydrogen phthalate. Phthalic acid was precipitated in quantitative yield. The residual material, after removal of solvent, evolved hydrogen bromide and afforded a liquid of higher boiling point than α -methyl- β -bromostyrene (XXVII), although the infrared spectrum

XXVII

of the material was consistent with its formulation as the latter compound. Elemental analysis indicated an excess of

bromine. Oxidation gave material which formed a 2,4-dinitrophenylhydrazone of melting point lower than that of acetophenone but not depressed by an authentic specimen of the latter. In a repetition, 102% of the theoretical yield of phthalic acid was obtained. In this experiment the dibromide was not isolated but dehydrobrominated with alcoholic potassium hydroxide. α -Methyl- β -bromostyrene was isolated in 20.5% yield, although the analytical figure for bromine was a little low in this case.

It appears then that in solvents of low polarity (those of high polarity were not investigated) bromine reacts with hydrogen phthalate esters of tertiary alcohols forming phthalic acid and a vicinal dibromide which may lose hydrogen bromide spontaneously. The reaction is slow unless at least one phenyl group is attached to the carbonyl carbon atom. It might be thought that the effect observed was merely one of spontaneous decomposition of the hydrogen phthalate to form an olefine and phthalic acid. The bromine could subsequently react with the olefine formed. Experiment showed however that when the hydrogen phthalates used were dissolved in carbon tetrachloride or chloroform without addition of bromine, phthalic acid was deposited only very slowly.

This interesting reaction does not appear to have been reported previously. The only parallel known to the present author is the reaction of tertiary alcohols with bromine^{99,100} to form a vic dibromide and water. In the latter reaction aliphatic alcohols react quite readily but in the presently discussed reaction the great enhancement of rate observed on introduction of a phenyl group suggests that the rate-determining step must be related to the ease of formation of a carbonium ion. However, the formulation of a mechanism will require a more complete investigation of this reaction.

Another possible parallel can be drawn from the observation of Dangyan¹⁰¹, i.e., that esters, with iodine or other halogen, in the presence of aluminium, magnesium, or iron give an alkyl halide.

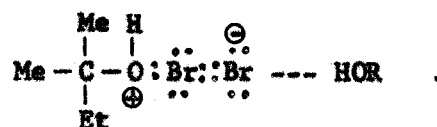
The reaction mentioned above, in which a tertiary alcohol and bromine form a dibromide and water, has been the

⁹⁹E.A. Braude and E.A. Evans, J. Chem. Soc., (1955) 3331.

¹⁰⁰W.L. Evers, H.S. Rothrock, H.M. Woodburn, E.E. Stahley, and F.C. Whitmore, J. Am. Chem. Soc., 55, 1136 (1933).

¹⁰¹M.I. Dangyan, Bull. Armenian Branch Acad. Sci. U.S.S.R., (1942) 7 - cf. Chem. Abs., 40, 3393 (1946).

subject of a few investigations. In the case of the reaction of t-amyl alcohol with bromine in carbon tetrachloride at 25°, the reaction is first order in bromine¹⁰². The authors believed that the rate-determining step involved reaction between a 1:1 complex of alcohol and bromine with a molecule of alcohol and proposed a possible intermediate:



Prilezhaev¹⁰³ investigated a wider range of alcohols and proposed that the first step was bromination of the alcohol to form a compound of the type $\text{R}_2\text{COH}-\text{CHBrR}'$. However, he was able to isolate the proposed intermediate only from 1,1-diphenylpropanol brominated with bromine in 80% aqueous acetic acid. In the case of aliphatic alcohols the vic dibromide was isolated.

For the present author's purposes it was of interest to see whether the decomposition of hydrogen phthalates would be catalysed by iodine. In a preliminary experiment dimethylphenylcarbinyl hydrogen phthalate was treated with iodine in

¹⁰²L.J. Andrews and R.M. Keefer, J. Am. Chem. Soc., **75**, 3557 (1953).

¹⁰³V.I. Ponevich-Kolyada and N.A. Prilezhaev, J. Gen. Chem. U.S.S.R., **21**, 571 (1951) (English translation).

chloroform; it deposited phthalic acid in 10⁴% yield overnight. A blank deposited only 4% phthalic acid under the same conditions. The other products were not investigated.

This reaction would appear to be worthy of further study. Rate studies could be carried out. The course of reaction could be followed by filtration and weighing of the phthalic acid produced. Three possibilities come into consideration.

- 1) That the bromine displaces the equilibrium of the decomposition reaction.
- 2) That an intermediate brominated hydrogen phthalate is formed.
- 3) That halogens specifically catalyse the reaction either by simultaneous attack of halogen and loss of phthalic acid or by loss of phthalic acid from an ester-bromine complex.

Attempted Extension to Silicon Series

Should it be possible to extend the above brominative cleavage reaction to the silicon series it would provide

a route to compounds containing the structure $\begin{array}{c} \text{Br} \quad \text{Br} \\ | \quad | \\ -\text{C}-\text{Si}- \end{array}$

which may possibly be debrominated or dehydrobrominated by

conventional methods. Gilman¹⁰⁴ has independently proposed the use of this type of compound prepared by the action of N-bromosuccinimide on an halogenosilane. However, the latter author reported that from $(C_6H_5)_2CBrSiBr(C_6H_5)_2$ only tetraphenylethylene or, in air, benzophenone, was isolated.

In the present author's studies severe difficulties were encountered owing to 1) the failure to prepare pure silyl hydrogen phthalates under the manifold conditions employed and 2) the tendency of bromine to detach aryl groups from silicon. The latter reaction has already been fully investigated¹⁰⁵ and has been shown to proceed with inversion of configuration¹⁰⁶.

In all of the present work involving silyl hydrogen phthalates the crude material was used. In a preliminary experiment diphenylmethylsilyl hydrogen phthalate was treated with bromine in carbon tetrachloride. After filtration to remove phthalic acid the filtrate showed in its infrared spectrum little difference from the unreacted material except that carbonyl and hydroxyl bands no longer appeared. On

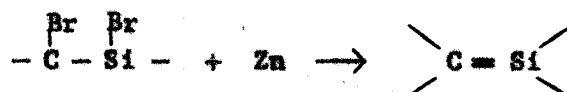
¹⁰⁴H. Gilman, in Proceedings of the Conference on High Temperature Polymer and Fluid Research, Dayton, Ohio, (1962), p. 175.

¹⁰⁵C. Eaborn and D.E. Webster, J. Chem. Soc., (1957) 4449.

¹⁰⁶C. Eaborn and O.W. Steward, Proc. Chem. Soc., (1963) 59.

evaporation of the extract a very small amount of pale yellow solid remained. This material fumed strongly with water. The melting point was about 45° but on attempted recrystallisation no pure material could be isolated. Apparently the material hydrolysed very readily.

In a repetition the crude silyl ester reacted rapidly with bromine in acetic acid. After filtration of phthalic acid zinc dust was added and the solution stirred, in the hope of bringing about a debromination reaction of the type shown below.

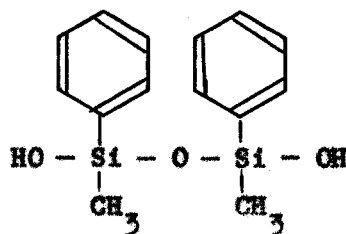


The product was then hydrolysed and separated. Bromobenzene was isolated from the products and a very dark liquid which was partially purified to an oil of composition $\text{C}_{5.36} \text{H}_{7.21} \text{SiO}_{2.145}$. Hence it appears that bromine had detached the phenyl groups at least as readily as it had split out phthalic acid.

In a further repetition bromobenzene was obtained plus a small quantity of benzene, presumably formed by reduction of the first formed bromobenzene. Small quantities of the material were distilled and the residue was purified by chromatography. The composition of the product corresponded to $\text{C}_{6.78} \text{H}_{8.04} \text{SiO}_{1.48}$ which was considered to be the compound

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XXVIII but the latter has been claimed^{92,107} to be a solid



XXVIII

melting at 111° or 112-113°.

To ascertain that the reactions under investigation were not reactions of unreacted chlorosilane, a portion of diphenylmethylchlorosilane was treated first with bromine in acetic acid and then with zinc. After stirring, water was added and the organic layer separated and dried. By distillation bromobenzene and benzene were isolated. The residue was rubbery in nature and had a very high melting point. After purification it had an analysis corresponding to the composition $\text{C}_{1.95} \text{H}_{5.47} \text{Si}_{1.00} \text{O}_{3.03}$.

Since reaction with immediate addition of zinc had given neither a compound containing a carbon-silicon double bond nor any hydrolysis product unequivocally corresponding

⁹²W.H. Daudt and J.F. Hyde, *op. cit.*

¹⁰⁷M.E. Shostakovskii, D.A. Kochkin, Kh.I. Kondra'tev, and V.M. Rogov, *Zhur. Obshchei Khim.*, 26, 3344 (1956) (English translation, p. 3721).

to the dibromide it was decided to investigate the course of the reaction without addition of zinc. After reaction with bromine the material was hydrolysed. Bromobenzene was again isolated along with small quantities of other volatile products. The residual material was a black oil that was not further investigated.

In a repetition using bromine in carbon tetrachloride bromobenzene was again obtained along with a black oil of composition $C_{6.29}H_{8.84}SiO_{4.02}$.

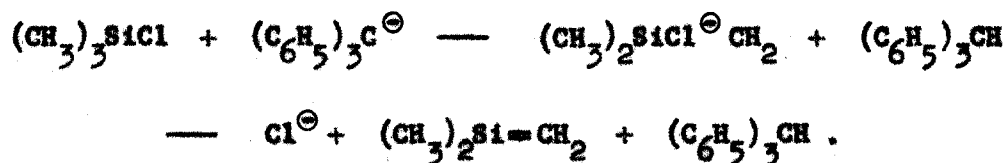
In each of the above cases a small amount of material, apparently benzene, was also obtained. An attempt was made to react trimethylsilyl hydrogen phthalate with bromine, but after six hours there was no evidence of reaction.

Attempted Reaction of Silyl Benzoates with Bromine

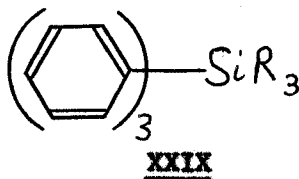
Since the benzoates could be prepared in a state of high purity it was of interest to see whether pure products could be isolated from the reaction of those esters with bromine. Crude diphenylmethylsilyl benzoate reacted very slowly with bromine in carbon tetrachloride, depositing benzoic acid. However after purification of the ester it did not react with bromine, not even in acetic acid. Trimethylsilyl benzoate did not react with bromine in acetic acid.

Reactions of Chlorosilanes with
Sodium Triphenylmethyl

Although bases such as quinoline and pyridine do not dehydrohalogenate chlorosilanes it appeared possible that a stronger base might do so. The use of sodium triphenylmethyl was investigated in the hope that it might bring about the following reaction:



This reaction has been previously investigated^{108, 109, 110} for a number of chlorosilanes and the sodium, potassium and lithium salts of triphenylmethane. The reaction affords a coupling product of the general formula XXIX but



¹⁰⁸ C.R. Hauser and C.R. Hance, J. Am. Chem. Soc., **73**, 5846 (1951).

¹⁰⁹ H. Gilman, A.G. Brook, and L.S. Miller, J. Am. Chem. Soc., **76**, 3757, 4531 (1953).

¹¹⁰ L.S. Miller, Ph.D. Thesis, Iowa State College, 1950.

since previous authors isolated these compounds in less than 50% yield the possibility remained that some unsaturated material might be isolated.

Ethereal solutions of sodium triphenylmethyl in concentrations of 0.1 to 0.2 N were prepared and added to an ethereal solution of chlorosilane with stirring. The first few ml. of base were decolourised without formation of any precipitate. After the first few ml. had been added, a yellow solution was formed along with deposition of a yellow precipitate. Previous authors¹⁰⁹ had then hydrolysed the mixture but in the present author's experiments the effect was first examined of dispensing with hydrolysis.

The precipitate which formed contained sodium, as both sodium chloride and unreacted sodium triphenylmethyl. Small quantities of material, apparently a mixture of hexaphenylethane and triphenylmethylperoxide were obtained.

In a reaction between trimethylchlorosilane and sodium triphenylmethyl, sodium chloride was obtained in 92.5% yield. Triphenylmethane was isolated in quantitative yield but no other identifiable product. In a repetition, sodium chloride was obtained in 82.1% yield. The residues were

¹⁰⁹H. Gilman, A.G. Brook, and L.S. Miller, op. cit.

gummy and extraction with 99% ethanol gave only gums and small quantities of material of very wide melting range.

The experiments were then repeated with hydrolysis after addition of sodium triphenylmethyl. As recommended by previous authors^{108,109,110}, the solids were extracted by ethanol. The residue could not be satisfactorily recrystallized from ethanol-ethyl acetate as recommended by the previous authors since the material was of very low solubility in this solvent pair. However a benzene-ethanol solvent pair proved very suitable and gave the compound $(\text{CH}_3)_3\text{SiC}(\text{C}_6\text{H}_5)_3$ in the same yield as previously reported¹⁰⁹. The structure was confirmed by quantitative hydrolysis to triphenylmethane¹¹⁰. In the aqueous layer, sodium chloride was present to the extent of 80% of theory. Again triphenylmethane was isolated but the other products were intractable gums of indefinite composition.

From the reaction of diphenylmethylchlorosilane with sodium triphenylmethyl only gums could be isolated.

¹⁰⁸ C.R. Hauser and C.R. Hance, op. cit.

¹⁰⁹ H. Gilman, A.G. Brook, and L.S. Miller, op. cit.

¹¹⁰ L.S. Miller, op. cit.

Resume and Conclusions

At no stage of this work was any evidence of a carbon-silicon double bond found, and during its course claims by other authors to have prepared such compounds were withdrawn. It is concluded that the existence of such bonds must be regarded as highly improbable, though there appears to be no convincing theoretical reason why they should be incapable of existence.

A new reaction, the brominative cleavage of tertiary carbonyl hydrogen phthalates, appears to be worthy of further study and its extension to include a study of the effect of iodine on such compounds would undoubtedly be fruitful.

CHAPTER IV - EXPERIMENTAL PROCEDURES

Hydrolysis of Chlorosilanes

Preparation of Diphenylmethylsilanol

(i) The addition of ice to a small portion of diphenylmethylchlorosilane (Dow Corning Silicones, purity >97%) resulted in a very slow reaction. When heated on a steam bath, a cloudy white upper layer was formed. Hydrochloric acid was shown to be present by the vigorous effervescence on addition of sodium bicarbonate solution. The upper layer was soluble in ether.

(ii) Diphenylmethylchlorosilane was hydrolysed with sodium bicarbonate solution. The silanol was extracted with ether. Most of the solvent was removed on a steam-bath; the last traces were removed in vacuo. A white oil remained.

To a solution of diphenylmethylsilanol in ether or benzene a solution of phthalic anhydride in the same solvent was added. No precipitate was formed, not even on addition of sodium bicarbonate.

On standing the diphenylmethylsilanol deposited white crystals, assumed to be sym-tetraphenyldimethyldisiloxane.

(iii) Diphenylmethylchlorosilane (50 g.) was heated with a saturated sodium bicarbonate solution (300 ml.) for three hours. Three layers were then present. Heating was continued for two hours, after which the lower layer had disappeared. On cooling the upper layer sank to the bottom. It was separated and the upper layer extracted with ether. The original lower layer and the ethereal extract were combined and dried over anhydrous sodium carbonate. The solvent was then removed in vacuo yielding a moderately turbid oil. On vacuum distillation a liquid appeared to be lost, though none could be collected. At a bath temperature of 31° (pressure 2.5 mm.) the liquid in the flask solidified to a white crystalline mass which was soluble in ether, benzene, acetone and petroleum ether. On crystallisation from ether it had melting range $32-48^{\circ}$ and was assumed to be sym-tetraphenyldimethyldisiloxane.

Preparation of Silyl Hydrogen Phthalates

(i) Diphenylmethylchlorosilane (5 g.) and potassium hydrogen phthalate (9 g.) were mixed in ether. After several

hours a waxy white solid was deposited. This was removed by filtration and was washed first with ether and then with benzene. The filtrate was evaporated in vacuo whereupon it deposited a white powder. This material was insoluble in benzene and petroleum ether but soluble in water, m.p. 190-194^o (dec.). It was tentatively identified as phthalic acid.

The neutralisation equivalent was determined in duplicate by solution in sodium hydroxide and back titration with hydrochloric acid as follows:

The material (0.2574 g.) was dissolved in 0.1029 N sodium hydroxide (60.00 ml.). 0.1088 N hydrochloric acid (28.18 ml.) was required for back titration. Neutralisation equivalent calculated, 82.8.

The material (0.1312 g.) was dissolved in 25.00 ml. of 0.1029 N sodium hydroxide, 9.12 ml. 0.1088 N hydrochloric acid being required for back titration. Neutralisation equivalent, 84.6.

Mean N.E. 83.7 (phthalic acid requires 83.1).

(ii) In all subsequent preparations all apparatus was dried overnight in the oven at 110^o (approx.). Diphenylmethylchlorosilane (58 g., 0.25 moles) in 50 ml. ether was added with stirring to a slurry of oven-dried potassium hydrogen phthalate (102 g., 0.5 moles) in 200 ml. sodium-dried

ether. Stirring was continued for one hour. The precipitate was then filtered and washed twice with ether, the filtrate and washings were then evaporated. The residue from filtration weighed 85 g. (calc. 70 g.). The residue was analysed for potassium hydrogen phthalate. The material (0.3385 g.) was dissolved in 0.1029 N sodium hydroxide (25.0 ml.) and then back titrated with 0.1088 N hydrochloric acid, 7.80 ml. being required. Assuming no phthalic acid to be present this corresponds to 0.3519 g. potassium hydrogen phthalate. Hence part of the residue consisted of phthalic acid. Calculation shows the figures to correspond to 2.7% phthalic acid and total potassium hydrogen phthalate in the residue to be 51.5 g. This indicates reaction to the extent of nearly 100%. The presence of chloride in this residue was indicated by a qualitative test.

The filtrate deposited, on standing, 12.5 g. white solid of m.p. 188-190° (dec.). The N.E. was determined using 0.3113 g. material, 50.00 ml. 0.1029 N sodium hydroxide, back titration requiring 17.46 ml. 0.1088 N hydrochloric acid. Hence neutralisation equivalent calculated is 95.2.

The filtrate was then evaporated whereupon more solid (8.4 g.) was deposited, m.p. 187-194°. After filtration of this, there remained 46.8 g. filtrate which reacted slowly

with bromine in carbon tetrachloride depositing more phthalic acid. The filtrate also decolourised alkaline potassium permanganate slowly. On hydrolysis and addition of silver nitrate to the filtrate, chloride ion was shown to be still present. On standing more phthalic acid was deposited.

It was found that syn-tetraphenyldimethyldisiloxane slowly decolourised bromine water but not bromine in carbon tetrachloride. Diphenylmethylchlorosilane slowly decolourised bromine in carbon tetrachloride and rapidly reacted with bromine in acetic acid.

At this point the filtrate was a clear viscous oil which did not solidify in ice. Filtration was repeated and distillation attempted. A very small amount of distillate was obtained, b.p. $160^{\circ}/10$ mm. This solidified in the refrigerator but partially remelted at room temperature. It had the odour of hydrogen chloride and gave a positive test for chloride ion with nitric acid and silver nitrate. On standing this material crystallised to a solid, m.p. $41.5-45^{\circ}$.

The original filtrate still deposited a solid, m.p. $201-206^{\circ}$ when treated with bromine in carbon tetrachloride. The melting point was not depressed by mixture with phthalic acid. The infrared spectra of the original filtrate before and after treatment with bromine were very similar except that after bromination the phthalate peak was not present.

The liquid obtained from the addition of bromine to the silyl ester was evaporated. A very small amount of pale yellow solid which fumed strongly with water remained. The aqueous filtrate was shown by qualitative tests to contain bromide ion.

(iii) A mixture of diphenylmethylchlorosilane (57.9 g., 0.25 mole), potassium hydrogen phthalate (102 g., 0.5 mole) and benzene (40 ml.) was shaken for 6 hours. This quantity of solvent proved to be too little since the mixture set to a hard mass. This solid was extracted with acetone and filtered giving 111 g. residue (theory 88.3 g. for complete reaction). The filtrate was evaporated in vacuo. The viscous material left, when hydrolysed with water, gave a positive test for chloride ion. With bromine in carbon tetrachloride reaction occurred rapidly depositing a white precipitate, m.p. 186-213° (dec.).

A portion was distilled at 139-140°/ 1 mm. yielding a pleasant smelling oily liquid. This distillate solidified in the refrigerator to a hard glass. The refractive index of the liquid at 18° was 1.5822 (but see below) (diphenylmethylchlorosilane, 1.5762). It gave a negative test for halogen and reacted very slowly with bromine in carbon tetrachloride or acetic acid. The molecular weight determined cryoscopically

in benzene was 170. Elemental analysis showed it to have the composition $C_{13}H_{14.25}SiO$. The compound was therefore diphenylmethylsilanol.

The distillate was redistilled yielding 12.5 g. (23.4%) of pure diphenylmethylsilanol, n_D^{25} 1.5802. Daudt and Hyde⁹² give b.p. 184-7°/24 mm., n_D^{25} 1.5777.

This silanol reacted very slowly with bromine in carbon tetrachloride but on evaporation of solvent only a very small quantity of heavy yellow oil remained. On cooling this solidified to a yellow solid, m.p. about 45°. The brominated material was very soluble in carbon tetrachloride, benzene, petroleum ether and acetone, but no pure product could be isolated after several attempts at recrystallisation.

(iv) A mixture of diphenylmethylchlorosilane (58 g., 0.25 mole), potassium hydrogen phthalate (53 g., 0.25 mole + 2 g. excess) and 80 ml. benzene was mechanically shaken for 21 hours. Filtration yielded a total of 31.5 g. solid (theory 20.9 g.). After filtration the residue was extracted with benzene and then acetone. On distillation of this filtrate before it had had time to deposit much solid a small amount of distillate, b.p. 125-150°/0.75 mm., was obtained. It had

⁹²W.H. Daudt and J.F. Hyde, *op. cit.*

the characteristic odour of hydrogen chloride and formed white fumes with ammonia. This was redistilled at 123-124°/0.7 mm., the distillate having $n_D^{23.5}$ 1.5798. Elemental analysis showed this to have the composition C, 73.28%; H, 6.76%; Si, 12.88%. $C_{13}H_{14}SiO$ requires C, 72.85%; H, 6.58%; Si, 13.09%. The infrared spectrum in carbon tetrachloride showed free hydroxyl at 2.65 μ , and hydrogen bonded hydroxyl at 2.87-3.1 μ . When this material was treated with hydrochloric acid, tetraphenyldimethyldisiloxane was formed.

(v) A mixture of diphenylmethylchlorosilane (58 g., 0.25 mole) and potassium hydrogen phthalate (102 g., 0.5 mole) was shaken in carbon tetrachloride (150 ml.) for 19 hours. A white solid (112.2 g.) was precipitated. Extraction of 3.2998 g. of this residue with acetone showed a loss of 1.2031 g. Assuming this to be phthalic acid, there is 41 g. in the whole residue. Titration of the acetone insoluble material with sodium hydroxide showed it to contain 83.4% of potassium hydrogen phthalate.

The filtrate was refluxed. On cooling, a precipitate appeared. This was filtered off and found to weigh 2.95 g., m.p. 177-183° (dec.), neutralisation equivalent, 166.7.

The filtrate was mixed with acetone for ease of filtration, filtered and the solvent was then removed in vacuo.

It was then distilled yielding a small amount of a liquid material, b.p. $170^{\circ}/1.25$ mm. and a solid, m.p. $126-131^{\circ}$. The latter material crystallised from chloroform in long needles, m.p. $129-132^{\circ}$. The melting point was not depressed by admixture with phthalic anhydride.

(vi) A mixture of diphenylmethylchlorosilane (58 g., 0.25 mole), potassium hydrogen phthalate (102 g., 0.5 mole) was mechanically shaken with carbon tetrachloride (300 ml.) for 17 hours. A solid (126.40 g.) was filtered off and then exhaustively extracted with carbon tetrachloride. After drying the residue at 100° , there still remained 93.5 g. of solid material (theory, 69.6 g.). The filtrate and carbon tetrachloride extract were combined, evaporated and then distilled. Much solid sublimed out and a liquid distillate (18 g.), b.p. $192-208^{\circ}/1$ mm., was obtained. This was filtered from sublimed solid. The liquid solidified to yield a compound, m.p. $39-43.5^{\circ}$. Recrystallisation from carbon tetrachloride yielded a compound, m.p. $45-49^{\circ}$, presumably tetraphenyldimethyldisiloxane.

(vii) A mixture of diphenylmethylchlorosilane (58 g., 0.25 mole) and potassium hydrogen phthalate (102 g., 0.5 mole) was mechanically shaken in carbon tetrachloride (300 ml.) for 19 hours. The precipitate was filtered off and exhaustively extracted with carbon tetrachloride. It then weighed 93.0 g.

(theory, 69.6 g.). The filtrate and combined carbon tetrachloride extracts were then evaporated to a viscous yellow oil. The neutralisation equivalent of this material was determined to be about 4000. The oil was then heated to reflux temperature and cooled. The solid which formed was filtered off (3.4 g.) and was identified as phthalic anhydride by a mixed melting point determination. On distillation of the filtrate, more solid, m.p. 120-124° (phthalic anhydride) sublimed out and a small liquid fraction, b.p. 183-189°/0.4 mm. was obtained. When treated with hydrochloric acid this material gave a solid, m.p. 44-48°, after crystallisation from benzene. The solid was thus identified as tetraphenyl-dimethyldisiloxane.

The liquid distillate had $n_D^{23.5}$ 1.5798 and was shown to contain active hydrogen by its reaction with methyl magnesium iodide. The liquid distillate was therefore diphenylmethylsilanol.

(viii) A mixture of diphenylmethylchlorosilane (38.75 g., 0.17 mole) and potassium hydrogen phthalate (68 g., 0.33 mole) was mechanically shaken with carbon tetrachloride (150 ml.) overnight. The residue was extracted with carbon tetrachloride and, after drying, weighed 61.19 g. This was extracted with acetone, which reduced it to 49.26 g. indicating

87% reaction. Calculation shows that this weight of residue, assumed to consist only of potassium hydrogen phthalate and potassium chloride should contain 74.5% potassium hydrogen phthalate. Titration with sodium hydroxide showed it to contain 74.5% potassium hydrogen phthalate. The acetone extract, on evaporation, afforded 11.09 g. phthalic acid, m.p. 189-196° (dec.).

The filtrate deposited a solid on standing in a vacuum desiccator. This was filtered off and recrystallised from water to a compound having m.p. 208-212° (dec.) (phthalic acid). Over a period of 21 days more phthalic acid was deposited.

A portion was distilled. Much phthalic anhydride sublimed out, and a fraction, b.p. 130-135°/0.7 mm., which solidified on standing was obtained. The undistilled residue was chromatographed on alumina, using benzene as eluent. Two fractions were collected of which the second gave, on evaporation of solvent, only a little brown material. The first, on evaporation, gave a fairly mobile yellow liquid of n_D^{24} 1.5831. Analysis showed it to be impure diphenylmethylsilanol.

Preparation of Diphenylmethylsilyl Benzoate

(1) A mixture of diphenylmethylchlorosilane (29 g., 0.125 mole), sodium benzoate (36 g., 0.25 mole) and carbon

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tetrachloride (200 ml.) was mechanically shaken for 19 hours. A hard white mass which weighed 40 g. was filtered off (theory, 25.3 g.). In water a solution of this material was acidic to litmus and on crystallisation deposited some solid, m.p. 114-118°, probably impure benzoic acid. The carbon tetrachloride filtrate reacted slowly with bromine in carbon tetrachloride.

The remainder of the carbon tetrachloride filtrate was evaporated and distilled in vacuo. A small amount of benzoic acid sublimed out and a large liquid fraction was obtained, b.p. 174-178°/0.5 mm. This was filtered from benzoic acid to give a halogen-free liquid, $n_D^{23.5}$ 1.5868. Analysis showed it to have the composition C, 74.70%; H, 6.07%; Si, 6.97% (calc. for diphenylmethylsilyl benzoate, $C_{20}H_{18}SiO_2$, C, 75.44%; H, 5.70%; Si, 8.80%). The infrared spectrum in chloroform showed it to be an ester and it was identified as impure diphenylmethylsilyl benzoate.

(ii) A mixture of diphenylmethylchlorosilane (58 g., 0.25 mole) and sodium benzoate (72 g., 0.5 mole) was mechanically shaken with benzene (400 ml.) for 19 hours. A white solid residue which weighed 63.5 g. was filtered off and extracted with benzene for 6 hours. A residue which weighed 56.6 g. was left after drying at 110°. This residue was acidic to litmus. Titration with sodium hydroxide showed 3.7%

benzoic acid to be present and precipitation of chloride as silver chloride showed 22% sodium chloride. This indicated that reaction had proceeded to the extent of 89%.

The original benzene extract and that obtained from the residue were combined and evaporated, yielding 61.8 g. material (theory, 79.5 g. ester) of neutralisation equivalent 362. Diphenylmethylsilyl benzoate has a calculated neutralisation equivalent of 318, hence this also indicated a yield of about 88%.

Hydrolysis of the ester with sodium hydroxide, followed by pouring onto a mixture of crushed ice and hydrochloric acid gave benzoic acid, m.p. 119-121°, not depressed by an authentic sample.

A portion (26 g.) of the above ester was refluxed for 2 hours. It turned dark in the process. On subsequent distillation a small amount of benzoic acid sublimed out but the largest portion distilled at 110-198°/0.75 mm. This was filtered to remove benzoic acid and redistilled. Two fractions were obtained. One (4.9 g.) boiled at 92-140°/0.35 mm., $n_D^{24.5}$ 1.5783. It gave a positive Beilstein's test for halogen. The second fraction (13.6 g.) of boiling range 182-189°/0.35 mm., $n_D^{24.8}$ 1.5877 was halogen-free. The neutralisation equivalent of the higher boiling fraction was 311. On

redistillation of this fraction a small fraction, b.p. 62-90°/0.25 mm., $n_D^{24.5}$ 1.5878 and a large fraction of boiling range 172-184°/0.25 mm., $n_D^{24.5}$ 1.5886 were obtained. Analytical figures showed C, 75.20%; H, 5.76%; Si, 8.43%. These figures are in agreement with those calculated (see above) for diphenylmethylsilyl benzoate.

After standing for several weeks the ester had deposited more solid which was filtered off and found, after recrystallisation from water, to have m.p. 111-118°. It was identified as impure benzoic acid. The filtrate was distilled. A little solid sublimed out and three fractions were obtained: i) b.p. 100-170°/0.5 mm.; ii) b.p. 172-176°/0.5 mm., n_D^{25} 1.5854; iii) b.p. 186-189°/0.5 mm., n_D^{25} 1.5868. Both fractions (ii) and (iii) were clear viscous liquids which did not decolourise bromine in carbon tetrachloride. The infrared spectra of fractions (ii) and (iii) were very similar and consistent with the formulation of the compound as diphenylmethylsilyl benzoate. Hydrolysis of a portion of the compound with sodium hydroxide followed by treatment with hydrochloric acid gave benzoic acid.

Fraction (iii) had the composition C, 75.51%; H, 5.99%; Si, 8.71%; calculated for diphenylmethylsilyl benzoate, C, 75.44%; H, 5.70%; Si, 8.80%.

Attempted Reaction of Diphenylmethylsilyl Benzoate
with Bromine

The impure benzoate ester (10 g.) was treated with bromine in carbon tetrachloride until excess bromine was present. It deposited benzoic acid in 89% yield, identified by mixed melting point with authentic material and by neutralisation equivalent. The residual gum was dissolved in petroleum ether which on evaporation gave again the yellow oil with a strong odour and which fumed in air.

On distillation a very small fraction, b.p. $97-101^{\circ}$ / 0.3 mm, was obtained along with a yellow fraction, b.p. 200° / 0.3 mm. This was shown by Beilstein's test to contain halogen but in a Lassaigne test showed only very little bromine present. Analysis showed this to have the composition C, 70.30%; H, 5.90%; Si, 15.24%; Br, 5.11%. On standing this material became a solid, m.p. $36-42^{\circ}$. Recrystallisation from petroleum ether yielded a compound, m.p. 49° . The melting point was not depressed on admixture with sym-tetraphenyldimethyldisiloxane. Hence the compound was probably a mixture consisting largely of diphenylmethylchlorosilane and diphenylmethylbromosilane. Since the pure benzoate ester did not react with bromine (see above) the formation of benzoic acid in the latter case may have been catalysed by unreacted chlorosilane or may have been an artifact of hydrolysis.

Attempted Preparation of Trimethylsilyl
Hydrogen Phthalate

(1) A mixture of trimethylchlorosilane (27.1 g., 0.25 mole) and potassium hydrogen phthalate (102 g., 0.5 mole) was mechanically shaken with benzene (300 ml.) for 17 hours. Filtration afforded 101.4 g. residue, reduced after air drying to 91.70 g. This was extracted with carbon tetrachloride for 3 1/2 hours, at the end of which time it still weighed (after oven drying) 91.70 g. Extraction with acetone reduced the weight to 79 g., indicating 71% reaction. From the acetone extract 13.1 g. of material, m.p. 181° (dec.), was obtained, neutralisation equivalent 85 (calculated for phthalic acid, 83).

The filtrate was evaporated yielding a pale yellow liquid which hydrolysed very readily in air. It did not undergo any visible change on boiling. On addition of bromine in acetic acid an immediate precipitate of phthalic acid, identified by mixed melting point, was obtained.

The ester on distillation yielded a first fraction, b.p. 118-126°/0.7 mm. This solidified on standing to a material, m.p. 36-41°. A second fraction, b.p. 128°/0.85 mm., was also obtained. The latter required heating with a free flame for distillation. This second fraction was a clear

liquid, n_D^{25} 1.4824, which reacted with bromine depositing phthalic acid. Analysis of the distillate showed it to contain only 1.47% silicon, hence its nature remains obscure.

(ii) A mixture of trimethylchlorosilane (54.3 g., 0.5 mole) and potassium hydrogen phthalate (204.2 g., 1.0 mole) was mechanically shaken with carbon tetrachloride (300 ml.) for 11 hours. On filtration, a residue (239.4 g.) was obtained. Extraction with carbon tetrachloride, followed by oven drying, reduced this to 197.2 g. Extraction with acetone further reduced it to 160 g. (theory, 138.3 g.). The filtrate and carbon tetrachloride extract were combined and evaporated, yielding 53.98 g. yellow oil. Distillation afforded a colourless liquid, b.p. 69-84°, $n_D^{25.5}$ 1.3912, and considerable solid, m.p. 130-132° (literature value for phthalic anhydride, 131°). The undistilled residue was filtered yielding a dark filtrate and a straw coloured residue which on washing with carbon tetrachloride became a white solid, m.p. 129-131°, not depressed by admixture with phthalic anhydride. Total yield of phthalic anhydride was 14.7 g.

The distillate was redistilled and afforded 8.89 g. of material, b.p. 85-98.5°, $n_D^{25.5}$ 1.3900. The infrared spectrum in chloroform showed no bands due to hydroxyl. On redistillation it had b.p. 87-97°, n_D^{24} 1.3888. A qualitative

test¹¹¹ for silicon, which involved fusion of the material with sodium peroxide and fusion mixture, followed by identification of silicate by the ammonium molybdate-benzidine method, gave a positive result. A Lassaigne test for halogen was negative. The material was less dense than water. It would be expected that this compound would be trimethylsilanol or hexamethyldisiloxane, the reported constants being respectively, b.p. 100°, density 0.8112, n 1.3880 and b.p. 100.5°, density 0.7619, n 1.3774¹¹². However analysis showed the composition to be C, 34.76%; H, 8.04%; Si, 12.79%. Trimethylsilanol requires C, 40.0%; H, 11.18%; Si, 31.09%. Hexamethyldisiloxane requires C, 57.56%; H, 7.24%; Si, 22.41%. Hence the nature of the product remains obscure.

The undistilled oil could be distilled under vacuum yielding 0.26 g. solid, m.p. 134°, and 8.0 g. yellow oil, b.p. 130-136°/0.75 mm. The latter showed a carbonyl band in its infrared spectrum. This solidified partially on standing but from carbon tetrachloride only phthalic acid could be isolated, identified by melting point, acidity, and formation of fluorescein on fusion with resorcinol and concentrated sulphuric acid.

¹¹¹H. Gilman, R.K. Ingham, and R.D. Gorsich, J. Am. Chem. Soc., **76**, 918 (1954).

¹¹²E.G. Rochow, "Chemistry of the Silicones" (2nd), Wiley, New York (1951), p. 184.

Preparation of Trimethylsilyl Benzoate

A mixture of trimethylchlorosilane (54.3 g., 0.5 mole) and sodium benzoate (108 g., 0.75 mole) was mechanically shaken with carbon tetrachloride (calcium chloride dried and redistilled) for 12 1/2 hours. Filtration afforded 99.7 g. residue which was reduced by acetone extraction to 69.5 g. (theory, 65.3 g.). The combined original filtrate and carbon tetrachloride extract when evaporated gave 72.3 g. yellow oil containing a little solid. This was filtered and the filtrate distilled. Two fractions were obtained:

- i) b.p. 70-81°/1.2 mm., n_D^{25} 1.4836 (14.73 g.);
- ii) b.p. 81°/1.2 mm., n_D^{25} 1.4847 (36.38 g.).

Both were shown by the sodium peroxide fusion, bensidine-ammonium molybdate test to contain silicon and the infrared spectra showed them to be probably trimethylsilyl benzoate. Hydrolysis afforded benzoic acid.

Analytical figures for the second fraction showed C, 62.01%; H, 7.13%; Si, 14.31%. For trimethylsilyl benzoate, $C_{10}H_{14}O_2Si$, calculated C, 61.84%; H, 7.26%; Si, 14.42%.

Anderson¹¹³ gives for this compound, b.p. 221°/760 mm., d_{20} 1.004.

¹¹³H.H. Anderson, J. Am. Chem. Soc., 74, 2371 (1952).

The ester (17.70 g.) was dissolved in 100 ml. glacial acetic acid and bromine (5 ml.) in glacial acetic acid (100 ml.) was added over half an hour with stirring. After six hours of further stirring there was no evidence of reaction.

Reaction of Tertiary Hydrogen Phthalates
with Bromine

Methylphenyl-n-propylcarbinyl hydrogen phthalate (9.5 g., 0.030 mole) supplied by Mr. J.M. Prokipcak of this laboratory was treated with bromine (1.8 ml., 0.031 mole) in carbon tetrachloride (200 ml.). Overnight a white solid was precipitated. This was filtered off and found to weigh 5.46 g. (theory, 5.04 g. for phthalic acid). Recrystallisation from water afforded 4.17 g. (82.5%) material, m.p. 204.5° (dec.), not depressed by phthalic acid.

More bromine in carbon tetrachloride was added to the filtrate but no more precipitate was formed. The red solution was washed successively with sodium bicarbonate solution and by 1 N sodium hydroxide solution. The material was still red and slowly liberated iodine from potassium iodide solution.

Carbon tetrachloride was distilled from the solution leaving 8.88 g. dark residual liquid (expected 6.86 g. dibromide).

On distillation two fractions were obtained:

- i) b.p. $100-106^{\circ}/2$ mm., n_D^{25} 1.5703 (3.0 g.);
- ii) b.p. $118^{\circ}/2$ mm., n_D^{25} 1.5778 (0.35 g.).

Both were shown by a Lassaigne test to contain bromine.

Analysis of fraction (i) showed C, 54.3%; H, 5.38%; Br, 40.52%.

$C_{11}H_{14}Br_2$ requires C, 43.16%; H, 4.61%; Br, 52.23%. Hence hydrogen bromide had been lost on standing.

A portion (2.00 g.) was dissolved in glacial acetic acid and zinc dust added. The upper layer was separated, washed with 0.1 N sodium hydroxide, separated and dried over calcium chloride. It was distilled at $> 250^{\circ}/760$ mm. and found to have the refractive index 1.5432 at 22° . It slowly reacted with bromine in carbon tetrachloride and rapidly with bromine in acetic acid. The expected compound, α -methyl- β -bromo- β -ethylstyrene does not appear to have been described previously. The debrominated product also appears to be undescribed (α -methyl- β -ethylstyrene) but it had λ_{\max} 243 μ , ϵ_{\max} 7,300. Since α -methyl- β -methylstyrene has λ_{\max} 244 μ , ϵ_{\max} 8,700, the compound was thought to be 84% pure. Analysis showed C, 81.44%; H, 8.44%. Calculated for $C_{11}H_{14}$: C, 90.36%; H, 8.44%. This corresponds to a mixture of 72% α -methyl- β -ethylstyrene and 28% α -methyl- β -bromo- β -ethylstyrene. Since the latter compound would also exhibit ultraviolet

absorption at about $244 \text{ m}\mu$, the identification of the products from this reaction appears to be reasonably well established.

Reaction of t-Butyl Hydrogen Phthalate with Bromine

Sodium triphenylmethyl in ether, prepared in the usual way⁷⁷ was added to t-butanol (6.82 g.) until a permanent red colour appeared. Phthalic anhydride (14 g.) was then added and stirring continued for 3 hrs., after which excess water was added. The mixture was stirred for a few more minutes, then the aqueous layer separated and poured over a mixture of crushed ice and hydrochloric acid. The gummy material which formed crystallised in a few hours, yielding 9.83 g. (48%) of crude ester. This was recrystallised from chloroform-petroleum ether to m.p. $83-85^\circ$ (lit. value, $86-88^\circ$ ⁷⁷). Recrystallisation from benzene-petroleum ether gave a light amber solid, m.p. $82-83.5^\circ$ (5.31 g.).

t-Butyl hydrogen phthalate (5.0 g.) was mixed with bromine (1.6 ml.) in carbon tetrachloride (80 ml.). No precipitate was formed immediately. On standing for 90 hours a precipitate (0.43 g.), m.p. $191-192^\circ$ (dec.), N.E. 84.8, was formed and filtered off. On standing for a further 48 hours

⁷⁷K.G. Rutherford, J.M. Prokipcak, and D.P.C. Fung, op. cit.

a further material (0.11 g.), m.p. 195-201°, was formed. On heating to reflux temperature more solid (0.4 g.) was formed. Hence total solid material precipitated was 0.94 g. or 23.7%. After filtration the solution was washed with water, sodium bicarbonate solution, and sodium hydroxide solution, then dried over calcium chloride. The carbon tetrachloride was then distilled off. A small amount of residue with the characteristic odour of a bromocompound was left but it did not lend itself to recovery by distillation.

Reaction of Diphenylmethylcarbonyl Hydrogen
Phthalate with Bromine

Diphenylmethylcarbonyl hydrogen phthalate (9.58 g.) kindly supplied by Mr. J.M. Prokipeak, was mixed with bromine (1.6 ml.) in carbon tetrachloride (150 ml.). A precipitate was formed at once and hydrogen bromide was evolved. After 24 hours the solution had become colourless. A further portion of bromine (0.2 ml.) in carbon tetrachloride (20 ml.) was added but was not decolourised. The mixture was filtered yielding 4.70 g. residue (theory, 4.60 g.). On drying there was obtained 4.25 g. or 90.4%. This material was recrystallised from water to m.p. 201-203°, not depressed by admixture with phthalic acid, and having N.E. 83.2. Hence it was phthalic acid.

The filtrate was an orange fuming liquid which liberated iodine from potassium iodide solution. It was washed with sodium hydroxide solution, followed by water, separated, and dried over calcium chloride. On standing this liquid became orange. It was repeatedly washed with sodium hydroxide and with water, then redried over calcium chloride. The carbon tetrachloride was removed by distillation leaving a black residue of high boiling point which weighed 5.42 g. (theory for α -phenyl- β -bromostyrene, 7.17 g.). In the refrigerator it solidified to a black mass containing some crystals, m.p. $37-40^{\circ}$. The material was dissolved in ether and ethanol added, whereupon a small amount of a black solid separated. This was filtered. The remaining solution was treated with decolourising charcoal, evaporated and then set aside in the refrigerator. The solution crystallised to a yellow crystalline mass. On recrystallisation from ethanol, light brown crystals (1.43 g.), m.p. $37-40^{\circ}$, were obtained. The melting point was raised by further recrystallisation from ethanol to $39.5-41^{\circ}$, then to $40-41.5^{\circ}$. Literature value (Beilstein) is 40° or 50° . Analysis showed C, 65.11%; H, 4.54%; Br, 30.53%; calculated for $C_{14}H_{11}Br$, C, 64.90%; H, 4.28%; Br, 30.82%.

The product was oxidised with acidic potassium permanganate. Ethanol was then added and the solution filtered. Water was added until precipitation occurred. The liquid was then heated, cooled, then distilled. The residue was extracted with ether which was then evaporated. A yellow oil remained which, with 2,4-dinitrophenylhydrazine sulphate in methanol gave a red crystalline material. Recrystallisation from ethyl acetate yielded a red crystalline material, m.p. $243-246^{\circ}$, not depressed by admixture with authentic benzophenone 2,4-dinitrophenylhydrazone.

In a further reaction t-butylcarbonyl hydrogen phthalate (3.63 g.) in carbon tetrachloride (70 ml.) was mixed with bromine (1 ml.) in carbon tetrachloride (70 ml.). A small amount (0.6672 g. - 24.6%) of precipitate was formed after 4 days, m.p. $196-199^{\circ}$ (dec.). After recrystallisation from water, the melting point was raised to 210° (dec.). The filtrate was washed with sodium hydroxide and water, separated and dried over calcium chloride. Carbon tetrachloride was removed by distillation. The residue was lachrymatory but no material could be isolated in sufficient quantity for identification.

Reaction of Dimethylphenylcarbinyl Hydrogen Phthalate
with Bromine

(1) Preparation of Dimethylphenylcarbinyl Hydrogen Phthalate. A Grignard reaction was carried out using bromobenzene (78.5 g., 0.5 mole) in ether (200 ml.), magnesium (12 g., 0.5 mole) in ether (100 ml.) and acetone (29 g., 0.5 mole) in ether (200 ml.). The reaction mixture was hydrolysed with dilute sulphuric acid. The yield of dimethylphenylcarbinol was 39 g. (58%), b.p. 86-91°/11 mm., $n_D^{23.5}$ 1.5230 (lit. value, n_D^{19} 1.5314).

Dimethylphenylcarbinol (15.1 g., 0.11 mole) was titrated with sodium triphenylmethyl in ether, stirred for half an hour, and phthalic anhydride (17 g., 0.12 mole) was added. Stirring was continued for half an hour. Water was then added, the aqueous layer then separated and poured onto a mixture of ice and concentrated hydrochloric acid. The yield was 25.6 g. (81.7%). Recrystallisation from a mixture of benzene, chloroform and petroleum ether gave 8.65 g. material, m.p. 74-94° (dec.). This was used without further purification.

Dimethylphenylcarbinyl hydrogen phthalate (5.41 g., 0.019 mole) was dissolved in carbon tetrachloride (100 ml.)

and a solution of bromine (1.2 ml., 0.0201 mole) in carbon tetrachloride (80 ml.) was added. A precipitate was formed immediately. After 48 hours the solution was pale yellow. Solid material (3.25 g.), m.p. 201° (dec.), was filtered off (theoretical yield, 3.16 g.). The filtrate was washed once with sodium bicarbonate solution, three times with sodium hydroxide, once with water, and then dried over calcium chloride.

Carbon tetrachloride was removed by distillation. A dark liquid residue remained which evolved hydrogen bromide. On distillation, a yellow distillate (15 g.), b.p. $132-136^{\circ}/3$ mm., refractive index n_D^{32} 1.5864 (literature value for α -methyl- β -bromostyrene, b.p. $105-106^{\circ}/9$ mm.), was obtained. Its infrared spectrum showed this to be the desired compound, α -methyl- β -bromostyrene. Analytical figures showed C, 51.92%; H, 4.24%; Br, 43.65%; calculated for C_9H_9Br , C, 54.85%; H, 4.60%; Br, 40.55%. Presumably some 1,2-dibromo-1-methyl-ethylbenzene was still present.

Oxidation with acidic or alkaline potassium permanganate gave a material which formed a 2,4-dinitrophenylhydrazone, m.p. $212-216^{\circ}$ (from ethyl acetate) which was not depressed by the 2,4-dinitrophenylhydrazone of acetophenone. Presumably it was a different crystalline modification.

(11) Dimethylphenylcarbinyl hydrogen phthalate (3.37 g., 0.0119 mole) was dissolved in a mixture of carbon tetrachloride (100 ml.) and chloroform (30 ml.). Bromine (0.8 ml., 0.013 mole) dissolved in chloroform (30 ml.) was added. After two days a white solid (1.93 g.), m.p. 205-208° (dec.), was filtered off (theoretical yield, 1.97 g. phthalic acid).

The carbon tetrachloride and chloroform were evaporated and approximately 2 ml. of a dark high boiling residue remained. A solution of potassium hydroxide prepared by dissolving 1.5 g. potassium hydroxide in 6 g. 99% ethanol and 0.5 ml. of water was added and the mixture was warmed on a steam bath. It was then subjected to steam distillation yielding a clear liquid denser than water. This was separated and dried over sodium sulphate.

On vacuum distillation a clear liquid (0.48 g.), b.p. 103-108°/11 mm., n_D^{24} 1.5742, was obtained (theoretical yield 2.34 g., percentage yield 20.5%). Analytical figures showed Br, 37.88% (calculated Br, 40.55%).

Reaction of Dimethylphenylcarbinyl Hydrogen
Phthalate with Iodine

Dimethylphenylcarbinol (15.78 g., 0.116 mole) was treated with 910 ml. 0.146 N sodium triphenylmethyl (theoretical

quantity, 795 ml.). Phthalic anhydride (17.51 g., 0.118 mole) was added and the mixture was stirred for 2 1/2 hours. Water (500 ml.) was then added and stirring continued for 3 hours. The aqueous layer was separated and poured onto a mixture of ice and hydrochloric acid. The white precipitate which formed was filtered, washed with water and dried. Recrystallisation from a chloroform-petroleum ether solvent pair gave 5.43 g. of the hydrogen phthalate, m.p. 103-108°.

Dimethylphenylcarbinyl hydrogen phthalate (0.5 g.) was dissolved in 13 ml. chloroform. Iodine which was dissolved in chloroform was added. A blank was also prepared, omitting iodine. After 50 hours the iodine containing mixture had precipitated 0.30 g. phthalic acid, the blank 0.01 g. (theoretical quantity, 0.29 g.). Hence it appears that iodine catalyses the decomposition of tertiary carbinyl hydrogen phthalates.

Reaction of Diphenylmethylsilyl Hydrogen
Phthalate with Bromine

(1) A mixture of diphenylmethylchlorosilane (58 g., 0.25 mole) and potassium hydrogen phthalate (102 g., 0.5 mole) was mechanically shaken with sodium-dried benzene (250 ml.) for 17 hours. Filtration via water aspirator gave a residue

which, after extraction with benzene weighed 93.2 g., reduced by extraction with acetone to 75.4 g.

The filtrate was evaporated in vacuo and found to weigh 75.8 g. (theory, 90.5 g.). This was dissolved in glacial acetic acid (20 ml.) and bromine (10 ml., 29 g.) in glacial acetic acid (20 ml.) added. Vigorous reaction set in with evolution of fumes. No precipitate formed until after half an hour. This was filtered off and found to weigh 4.0 g., m.p. approximately 130° , presumably phthalic anhydride. After recrystallisation from water the melting point rose to 215° . It was not depressed by admixture with phthalic acid. The yellow solution did not liberate bromine from potassium iodide solution.

On this occasion no attempt was made to isolate the bromo-compound. Zinc dust (10 g.) was added and the solution was stirred for 1 1/2 hours. On filtration, a small amount of white material remained in the flask. This dissolved in water and with dilute nitric acid and silver nitrate gave a light yellow precipitate, suggesting that it was zinc bromide.

The filtrate was stirred with water for 2 1/2 hours and left to stand overnight. It was stirred with water again, separated, washed twice more with water, and separated. The aqueous layer was acidic to litmus. The organic layer

contained a small amount of white solid, m.p. 242-262°. This was removed by filtration. The organic layer was dried over sodium sulphate and distilled. A fraction weighing 11.2 g., b.p. 160°, n_D^{26} 1.5538, was collected. This was shown to be bromobenzene by bromination with bromine and iron to p-dibromobenzene, m.p. 85-88° (lit. value, 86.9°), nitration to 2,4-dinitrobromobenzene, m.p. from ethanol 70° (giving a strong Janowski's reaction) and by the identity of infrared spectrum of the material with that of authentic bromobenzene.

On distillation of the residue a small amount of material, b.p. 125°/0.6 mm. and another small fraction, b.p. 125°/0.6 mm. were obtained.

The undistilled residue was a very dark brown liquid (9.5 g.) which gave a very faint Beilstein test for halogen. The infrared spectra showed the undistilled residue and the two fractions to be of similar composition. The residue was dissolved in chloroform-petroleum ether. A small amount of solid material was removed by filtration. After repetition of the latter procedure and evaporation of solvent, a thick yellow oil (8.81 g.) was obtained. The infrared spectrum of this material showed no hydroxyl bands. Analysis showed the composition to be: C, 48.01%; H, 5.42%; Si, 20.93%. This corresponds to a formula $C_{5.36}H_{7.21}Si_{2.145}$. Hence the

bromine appears to have detached phenyl groups rather than to have formed a compound containing a carbon-silicon double bond.

(ii) A mixture of diphenylmethylchlorosilane (58 g., 0.25 mole), potassium hydrogen phthalate (102 g., 0.5 mole) and dry carbon tetrachloride (250 ml.) was shaken for 16 hours. After filtration the residue was extracted with benzene for 5 1/2 hours, after which the residue weighed 98.90 g. Extraction with acetone reduced this to a weight of 77.95 g. (corresponding to 74.2% reaction). A small amount of solid precipitated in the filtrate.

The above ester (59.4 g.) was dissolved in glacial acetic acid (50 ml.) in a three-necked flask fitted with reflux condenser, dropping funnel and stirrer. The flask was cooled in an ice bath and a solution of bromine (10 ml.) in acetic acid (50 ml.) was added dropwise over a period of half an hour. A precipitate was formed and there was much fuming. The liquid was filtered through a sintered glass funnel yielding, after drying, 9.62 g. residue, m.p. 199-207°. After recrystallisation from water the melting point was increased to 213° (dec.). The weight of this material plus that extracted by acetone is quantitative for phthalic acid.

To the filtrate zinc dust (10 g.) was added and the mixture was stirred. Vigorous reaction occurred and after

1 1/2 hours stirring the mixture was allowed to stand overnight. A very small amount of a solid precipitated. This was removed by filtration. Water (200 ml.) was added to the filtrate and stirring was continued for 2 hours. The layers were then separated. The organic layer was washed twice with water, once with saturated sodium bicarbonate solution and twice more with water. The aqueous layer was then neutral to litmus. The lower brown organic layer was separated and dried over sodium sulphate. The liquid was distilled giving a cloudy distillate (6.18 g.), b.p. 87-148° and a clear liquid (13.02 g.), b.p. 148-153°. Both were dried over sodium sulphate and subjected to fractional distillation. From the combined fractions were obtained 2.4 g. liquid, b.p. < 140°, n_D^{27} 1.4907 and a fraction (11.9 g.), b.p. 150-156°, n_D^{27} 1.5557 (literature values for bromobenzene, b.p. 155-156°, n_D^{25} 1.5598). The lower boiling fraction was redistilled yielding 1.46 g. liquid, b.p. 76-80°, n_D^{27} 1.4858, of the odour of benzene.

The higher boiling material was identified as bromobenzene by conversion (using bromine and iron) to p-dibromobenzene and by nitration to 2,4-dinitrobromobenzene, m.p. from ethanol 72-73° (literature value 75°).

The lower boiling material was nitrated with fuming nitric acid and concentrated sulphuric acid, yielding m-dinitro-

benzene, m.p. from ethanol 89-90°, not depressed by an authentic specimen. Hence the lower boiling material was identified as benzene.

On attempted vacuum distillation of the residue three small fractions of amber coloured material were obtained:

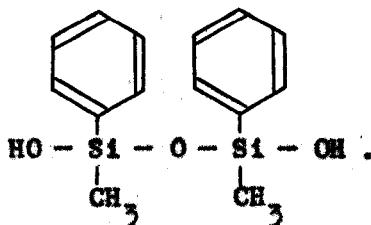
- i) b.p. 94-120°/0.35 mm., n_D^{26} 1.5667;
- ii) b.p. 172-236°/0.35 mm., n_D^{26} 1.5658;
- iii) b.p. 246°/0.4 mm.

Fractions (i) and (ii) burned with a smoky flame and were shown by Beilstein's test to contain halogen. Fraction (ii) appeared to form an oil when treated with 0.1 N sodium hydroxide but nothing could be crystallised from ether. There appeared to be no reaction with acid.

The remainder of the undistilled residue, a dark liquid of weight 0.14 g., was dissolved in carbon tetrachloride and petroleum ether was added until precipitation occurred. It was then allowed to cool in the refrigerator. A small amount of dark solid was filtered off. The solvent was evaporated and the residue was recrystallised from a carbon tetrachloride-petroleum ether solvent pair. After further filtration and evaporation a viscous brown oil was left. This was dissolved in chloroform and chromatographed on alumina using benzene as eluent. Five yellow fractions of approximately 75 ml. each

were collected. After evaporation of fraction (i) no significant quantity of product remained; fraction (ii) yielded 5.02 g. light brown liquid, n_D^{24} 1.5438; fraction (iii) yielded 0.64 g. light brown liquid, n_D^{24} 1.5403. Fractions (iv) and (v) yielded only small quantities of gum.

Fraction (ii) gave negative Beilstein's and Lassaigne tests for halogen. The analytical figures showed a composition C, 57.64%; H, 5.74%; Si, 19.83%. These figures correspond to a formula $C_{6.78}H_{8.04}Si_{1.48}$, and the compound might be formulated



However the latter compound is described^{92,107} as a solid melting at approximately 110°.

Reaction of Diphenylmethylchlorosilane with Bromine

Diphenylmethylchlorosilane (58.1 g., 0.25 mole) was dissolved in glacial acetic acid (60 ml.) in a three-necked

⁹²W.H. Daudt and J.F. Hyde, op. cit.

¹⁰⁷M.E. Shostakovskii, D.A. Kochkin, Kh.I. Kondra'tev, and V.M. Rogov, op. cit.

flask which was fitted with a reflux condenser, a dropping funnel and a stirrer. Bromine (13.6 ml., 40 g., 0.25 mole) in glacial acetic acid (60 ml.) was added dropwise with stirring over two hours. The flask became warm. Stirring was continued for one hour. Zinc (15 g.) was added with slow stirring whereupon the flask became hot and was cooled in ice-water. Stirring was continued for 3 1/2 hours. Water (200 ml.) was added and stirring was continued for an additional 2 1/2 hours. The lower layer was separated, washed with water, sodium bicarbonate solution, then twice with water, after which the aqueous layer was neutral to litmus. The lower yellow layer was separated and dried over sodium sulphate.

The dried liquid was distilled giving two fractions: (i) of b.p. 71-81° and (ii) of b.p. 149°. After redrying over sodium sulphate the two were fractionally distilled yielding two further fractions:

- I) 5.11 g., b.p. 78-81°, n_D^{26} 1.4951 (lit. value for benzene, n_D^{20} 1.5014);
- II) 11.72 g., b.p. up to 151°, n_D^{26} 1.5402 (lit. value for bromobenzene, n_D^{20} 1.5598).

Fraction (I) was nitrated with concentrated sulphuric acid and fuming nitric acid to yield m-dinitrobenzene, m.p. 85-86°

(from ethanol). The melting point was not depressed by an authentic specimen. Hence fraction (I) was identified as benzene. Fraction (II) was brominated using bromine and iron to yield p-dibromobenzene. After two recrystallisations from ethanol the melting point was 86-87.5°. It was not depressed by admixture with an authentic specimen. Hence fraction (II) was identified as bromobenzene.

The gummy residue from the distillation weighed 23.9 g. and was a pale brown rubbery material containing a small amount of dark material. It was partially soluble in acetone, benzene and carbon tetrachloride but not in petroleum ether or ethanol. Its melting point was greater than 280°. The material was washed with acetone, filtered, then washed with benzene and refiltered. After three more washings with acetone, followed by filtration, the material was a very pale brown gum. It was washed three more times with acetone, each washing being followed by filtration via water aspirator. The final product was a nearly colourless gum.

The residue was dried at 130° to constant weight at 5.03 g., being then a pale brown fairly hard gum with m.p. higher than 280°. Analysis showed its composition to be C, 22.21%; H, 5.27%; Si, 26.59%. This corresponds to a formula $C_{1.95}H_{5.47}Si_{1.00}O_{3.03}$ and hence the bromine must have detached

nearly all the phenyl groups from the compound with, presumably, formation of a cross-linked polymer.

The acetone washings, on evaporation, gave 2.72 g. of a soft gummy material.

(11) Diphenylmethylchlorosilane (58.1 g., 0.25 mole) was dissolved in glacial acetic acid (50 ml.) and bromine (40 g., 0.25 mole) in glacial acetic acid (50 ml.) was added over a period of two hours with stirring. Stirring was continued for 1 1/2 hours after which water (200 ml.) was added and the solution was stirred for an additional 2 hours. The two layers were separated and the organic layer was washed with water, sodium bicarbonate solution, twice with water until neutral to litmus, then dried over calcium chloride.

The product was distilled giving a small amount of cloudy material, b.p. 60-70°, along with a large fraction, b.p. 150-151°. Both were redried over calcium chloride, then combined and redistilled. Three fractions were obtained:

- (i) 0.6 g., b.p. 73-82°, n_D^{26} 1.4981;
- (ii) 23.08 g., b.p. 150-154°, n_D^{26} 1.5556;
- (iii) 3.03 g., b.p. not recorded because of slow distillation.

Fraction (i) was treated with bromine and iron rust, then poured into sodium carbonate solution, but only a small

quantity of insoluble liquid was formed. Attempted nitration of this fraction gave only an oil.

Fraction (ii) was brominated with bromine and iron rust, then poured into sodium carbonate solution. The white solid which formed was filtered off and recrystallised from ethanol. Its melting point was greater than 100° and was depressed on admixture with an authentic sample of p-dibromobenzene. On redistillation fraction (ii) gave 17.07 g. of material, b.p. $152-154^{\circ}$, n_D^{25} 1.5569. Bromination in the same manner gave a compound with melting point (after two recrystallisations from ethanol) of approximately 160° . The infrared spectrum of fraction (i) was identical with that of bromobenzene. Fraction (ii) was redried over sodium sulphate and redistilled, b.p. $153-154^{\circ}$, n_D^{25} 1.5573. It was identical with that of stock bromobenzene, though at slight variance with the literature value. Analysis showed the bromine content of fraction (ii) to be 50.73% (calculated for bromobenzene, C_6H_5Br , Br 50.92%).

Further bromination of fraction (ii) yielded a white crystalline product of melting point (after two recrystallisations from ethanol) $180-181^{\circ}$. Analysis showed this to be of the composition C, 18.53%; H, 0.36%; Br, 81.07%. This corresponds to a formula $C_{6.0}H_{1.39}Br_{3.95}$. Hence the material was 1,2,4,5-tetrabromobenzene, recorded m.p. 180° .

Nitration of fraction (ii) yielded a yellow solid of melting point $65-66^{\circ}$ after two recrystallisations from ethanol. It was not depressed on admixture with authentic 2,4-dinitrobromobenzene. Hence fraction (ii) was identified as bromobenzene.

Distillation of the original residues was continued, yielding 2 g. more material, b.p. $130-153^{\circ}$, and a small amount of material, b.p. $108-160^{\circ}/0.5$ mm. The black viscous residue was dissolved in benzene, treated with decolourising charcoal and filtered. On removal of solvent, a black viscous oil (16 g.) which contained halogen was formed. On treatment with 50 ml. of 20% sodium hydroxide solution a pale brown slurry was formed. This material was not further investigated.

(iii) Diphenylmethylchlorosilane (58.1 g., 0.25 mole) was dissolved in carbon tetrachloride (50 ml.) and a solution of bromine (14 g., 0.25 mole) in carbon tetrachloride (50 ml.) was added dropwise over a period of two hours with stirring. The mixture became warm. Stirring was continued for $3 \frac{1}{2}$ hours, then water (100 ml.) was added and stirring continued for an additional hour. Overnight two pale yellow layers were formed. These were separated; the lower layer was washed with water, then with 5% sodium hydroxide solution. The lower layer was then washed twice with tap water and three

times with distilled water until the aqueous layer was nearly neutral to litmus. The lower layer was separated and dried over calcium chloride. The material, a yellow liquid, was then distilled yielding a cloudy liquid, b.p. 74° , and a further cloudy liquid, b.p. 149° . Both were dried over calcium chloride. The residual material was subjected to steam distillation affording a dense liquid (small amount) which was separated and combined with the higher boiling material. Both were dried over sodium sulphate. On distillation a small amount of material, b.p. approximately 80° , was obtained. The main portion of the distillate was a liquid (15.06 g.), b.p. $150-154^{\circ}/746$ mm., n_D^{25} 1.5560. Bromination to p-dibromobenzene identified this material as bromobenzene.

The residue from the steam distillation was treated with 10% sodium hydroxide solution. It became semi-solid and was partially soluble in acetone and soluble in carbon tetrachloride. After removal of solvent it weighed 21.8 g. It was dissolved in acetone (100 ml.) and water (100 ml.) was added. A black oil was formed. This oil was separated and dried in vacuo. A Lassaigne test showed only a trace of halogen present. Analysis showed the composition to be C, 42.77%; H, 5.04%; Si, 15.86%. This corresponds to a formula $C_{6.29}H_{8.84}Si_{4.02}$, and hence the nature of the product is obscure. Presumably one phenyl group was detached.

Reaction of Trimethylchlorosilane with
Sodium Triphenylmethyl

A solution of sodium triphenylmethyl in ether was added to trimethylchlorosilane (9.64 g., 0.089 mole) until a permanent red colouration remained. An orange precipitate was formed and filtered off (in contrast to previous authors^{108,109,110} who hydrolysed the mixture at this point). The precipitate was orange-yellow, not melting at temperatures up to 190°. This gave a flame test for sodium and left a residue containing sodium on ashing. The precipitate was boiled with water and filtered; the filtrate was not alkaline to litmus or phenolphthalein. The residue was yellow, m.p. 164-170°. After recrystallisation from benzene, the melting range was raised to 178-179°. After a further recrystallisation from benzene the melting point was 178°. This material was designated product 'F'.

The filtrate obtained from hydrolysis of the precipitate was evaporated. A pink solid was deposited and was shown by precipitation of silver chloride to contain 60.5% chloride (calculated for sodium chloride, 60.5%).

¹⁰⁸C.R. Hauser and C.R. Hance, op. cit.

¹⁰⁹H. Gilman, A.G. Brook, and L.S. Miller, op. cit.

¹¹⁰L.S. Miller, op. cit.

Product 'F' was insoluble in water, only very slightly soluble in ether, insoluble in hydrochloric acid, sodium bicarbonate solution and sodium hydroxide solution. Attempts to detect a carbonyl group were negative. It was insoluble in petroleum ether and did not react with bromine in carbon tetrachloride. A Lassaigne test for halogen was negative. It was slightly soluble in concentrated sulphuric acid with the production of a yellow colour. This would appear to indicate the presence of a triphenylmethyl group, or triphenylcarbinol, but it cannot be the latter compound which melts at 162.5° and is very soluble in ether. Analysis showed product 'F' to have the composition C, 84.91%; H, 5.85% (mean of two determinations). This corresponds to a formula $C_{12.18}H_{10}O$. The M.W. was determined cryoscopically to be approximately 280. The properties would appear to be in accordance with those of triphenylmethylperoxide, described¹¹⁴ as having m.p. 185° , soluble in concentrated sulphuric acid with production of a yellow colour which darkens rapidly. The most probable interpretation is that the material was a mixture of hexaphenylethane (m.p. $145-7^{\circ}$ dec.) and triphenylmethyl peroxide.

¹¹⁴M. Gomberg, J. Am. Chem. Soc., 22, 757 (1900).

On standing, the ethereal filtrate of the original material deposited crystals of indefinite melting point (from benzene). This was probably the double compound of benzene and triphenylmethane.

(ii) Trimethylchlorosilane (1.2 g., 0.01 mole) in ether (10 ml.) was added to sodium triphenylmethyl in ether. No immediate precipitate was formed but on standing a pink solid was deposited. This was filtered off (0.65 g.) and hydrolysed to yield 0.065 g. of a yellow solid. The aqueous extract was alkaline to litmus and contained chloride ion. The ethereal extract deposited a yellow precipitate, m.p. $> 170^{\circ}$. After crystallisation from ethanol-ethyl acetate (1:2 by volume), the melting range was $224-229^{\circ}$ which eliminated trimethyl-(triphenylmethyl)-silane as a possible product^{109,110}.

(iii) Trimethylchlorosilane (10.85 g., 0.1 mole) was dissolved in ether (100 ml.) and 0.12 N sodium triphenylmethyl in ether (900 ml.) was added (theoretical quantity, 833 ml.). This corresponds to 29.4 g. sodium triphenylmethyl. The addition of the first few ml. of base resulted in decolourisation but no precipitate was formed. After further addition of a few ml. the solution became yellow and a precipitate was

¹⁰⁹H. Gilman, A.G. Brook, and L.S. Miller, op. cit.

¹¹⁰L.S. Miller, op. cit.

formed. Stirring was continued over 1 1/2 hours then the mixture was allowed to stand overnight. Filtration then yielded 8.00 g. of dark grey-yellow residue which partially melting at 250°.

This residue was boiled with water (50 ml.) and filtered. The filtrate was neutral to litmus but alkaline to phenolphthalein. Titration with hydrochloric acid showed 0.004 g. sodium hydroxide present. Precipitation as silver chloride showed the aqueous extract to contain 5.42 g. of sodium chloride (92.5%), the loss of weight on water extraction being in reasonable agreement with this (5.94 g.).

The ethereal filtrate was evaporated, affording 36.5 g. residue, m.p. 73-80°. This was extracted with 95% ethanol¹⁰⁹ for 5 hours. A residue, designated material 'B' (4.36 g.) of m.p. 146-164°, was left. The ethanolic extract, on evaporation, afforded a light brown solid, designated material 'C' (29.93 g.), m.p. 82-89°. (Theoretical quantity of triphenylmethane was 24.4 g. plus some from excess sodium triphenylmethyl.) This product was crystallised from a 1:2 mixture (by volume) of ethanol-ethyl acetate. Its melting point was then 80-92°. Recrystallisation from benzene gave material, m.p. 72-87°. This was recrystallised from benzene

¹⁰⁹H. Gilman, A.G. Brook, and L.S. Miller, op. cit.

to a material which crystallised in rhombohedra, m.p. 73-91.5°. After drying in a vacuum desiccator overnight the melting range was 90-95°. After many recrystallisations from benzene material 'C' weighed 15.26 g. and after vacuum drying for 5 hours, 10.38 g. Hence percentage benzene was calculated to be 31.9%. It seemed that this might be the 1:1 compound formed between benzene and triphenylmethane, for which the calculated percentage of benzene is 24.2%. The vacuum dried material was crystallised from petroleum ether, from which it crystallised as long needles, m.p. 91-97°. The infrared spectrum showed it to be probably triphenylmethane. Analysis showed its composition to be C, 93.75%; H, 6.55%; Si, 0.12% (triphenylmethane, $C_{19}H_{16}$, calculated C, 93.4%; H, 6.61%). A mixed melting point determination with triphenylmethane showed the two to be identical.

Product 'A' was recrystallised from benzene as plates, m.p. 160-169°, from ethanol-ethyl acetate, 155-172°. This was raised by a further recrystallisation from the same solvent to 166-177°. Product 'B' was only slightly soluble in 1:2 by volume ethanol-ethyl acetate. The melting range was 148-163°. On recrystallisation from benzene the melting range rose to 170.5-195°. Products 'A' and 'B' were not further investigated.

(iv) Trimethylchlorosilane (10.85 g., 0.1 mole) was dissolved in ether (100 ml.) and 0.111 N sodium triphenylmethyl in ether (950 ml., theoretical quantity 900 ml.) was added dropwise with stirring. As before, no precipitate was formed initially but precipitation occurred after addition of a few ml. base. Stirring was continued for 2 hours and the precipitate was filtered off. It was a pinkish solid which turned white on drying via water aspirator. The dry weight was 6.38 g. This was boiled with water and filtered, leaving a small amount of yellow residue.

The filtrate, when titrated with hydrochloric acid, was found to contain 0.287 g. sodium hydroxide. Complete evaporation of the aqueous extract yielded 5.27 g. solid (corrected for the portion used in titration). Hence the balance, assumed to be sodium chloride, was 4.98 g. (theory, 5.86 g.). Gravimetric estimation of chloride in the residue showed the presence of 4.8 g. sodium chloride.

The ethereal solution was evaporated to a semi-solid mass which weighed 45.28 g. This was extracted with 99% ethanol for 5 hours. The residue (still semi-solid) weighed 22.66 g. and was partially soluble in 1:2 by volume ethanol-ethyl acetate. On standing, a solution in this solvent deposited 0.69 g. white crystalline solid, m.p. 230-237°, from a dark brown liquid. The material which was insoluble

in the ethanol-ethyl acetate mixture was yellow, weighed 3.4 g. and melted at 170-172°. This was recrystallised from carbon tetrachloride to yield 1.50 g. material, m.p. 178-179°. Recrystallisation from a 1:1 by volume benzene-carbon tetrachloride solvent pair changed the melting point to 170-171°. Analysis showed its composition to be C, 86.54%; H, 5.90%; Si, 1.40%. This appears to be impure triphenylcarbinol, m.p. 162.5°, of calculated elemental analysis C, 87.6%; H, 6.15%. The 0.69 g. material which was deposited from the ethanol-ethyl acetate mixture was recrystallised twice to m.p. 238-240°. Analysis showed this to have the composition C, 90.04%; H, 6.37%; Si, 0.52%. This would appear to be impure triphenylmethane or triphenylcarbinol.

(v) Trimethylchlorosilane (21.67 g., 0.2 mole) was dissolved in ether (250 ml.) and 0.267 N sodium hydroxide in ether (750 ml.) was added dropwise with stirring over 1 hour. Initially the solution was decolourised without formation of a precipitate but after 20 ml. of ethereal sodium triphenylmethyl had been added a precipitate was formed and the solution became yellow in colour. After 650 ml. of solution had been added no further colour change was apparent. The reaction mixture was stirred for a further hour, at the end of which time the mixture was blood-red in colour. Water (200 ml.)

was then added (cf. ^{109,110}) and the reaction mixture was stirred for an additional 3 hours. The layers were then separated and the ethereal layer was dried over sodium sulphate. Ether was then evaporated using a rotating solvent stripper, leaving 80 g. pasty yellow solid. This was extracted in a Soxhlet extractor, using 99% ethanol (300 ml.) for 22 hours. There then remained 11.5 g. pale yellow residue, m.p. 141-156°. In contrast to the reports of Gilman and Miller^{109, 110} this was not completely soluble in 1:2 by volume ethanol-ethyl acetate but most of it dissolved giving a yellow solution. It was recrystallised to 3.81 g. yellow solid, m.p. 157-165°. Recrystallisation from 65 ml. 1:2 ethanol-ethyl acetate using decolourising charcoal gave white crystals, m.p. 157-165°. After a further recrystallisation from the same solvent (30 ml.) the melting range was 161-165°. After three more recrystallisations from an ethanol-ethyl acetate solvent pair the melting point was 159-164°. Recrystallisation from a chloroform-ethanol solvent pair gave a material still of wide melting range, 163-173°. Recrystallisation from benzene gave 1.37 g. material, m.p. 168-183°. Further recrystallisation from a benzene-ethanol solvent pair gave 1.15 g. material, m.p. 168-

¹⁰⁹H. Gilman, A.G. Brook, and L.S. Miller, op. cit.

¹¹⁰L.S. Miller, op. cit.

170°. Analysis showed this to have the composition C, 84.83%; H, 7.71%; Si, 5.11% [calculated for trimethyl-(triphenylmethyl)-silane, Si, 8.87%]. Hence the material was not pure $(\text{CH}_3)_3\text{SiC}(\text{C}_6\text{H}_5)_3$. Hydrolysis of the material (0.5 g.) with acetone (10 ml.) and 40% potassium hydroxide (10 ml.)¹¹⁰ gave 0.36 g. material which when recrystallised from petroleum ether yielded a product, m.p. 92-93.5° (mixed melting point with triphenylmethane 90-93°).

The impure material was recrystallised from a benzene-ethanol solvent pair and found to have m.p. 169-171°. This latter solvent was found to be a much better solvent than 1:2 by volume ethanol-ethyl acetate. Analysis showed this to have the composition C, 83.59%; H, 7.64%; Si, 8.22% [calculated for $(\text{CH}_3)_3\text{SiC}(\text{C}_6\text{H}_5)_3$, C, 83.53%; H, 7.60%; Si, 8.87%].

After the benzene-ethanol solution had stood in the refrigerator for 8 days a colourless crystalline material, m.p. 171-173° (Gilman, Brook and Miller¹⁰⁹ give 172-173°) was deposited. This made the total yield of trimethyl-(triphenylmethyl)-silane 7.51 g. or 12% (Miller¹¹⁰ reports 13.6%).

¹⁰⁹H. Gilman, A.G. Brook, and L.S. Miller, op. cit.

¹¹⁰L.S. Miller, op. cit.

Analysis of this last fraction showed Si, 8.94%.

In this run the aqueous extract was found by titration with standard acid to contain 0.426 g. sodium hydroxide, corresponding to 40 ml. excess base. Evaporation of the aqueous extract showed a total of 12.168 g. solid and hence 11.74 g. sodium chloride (expected 14.6 g.).

The ethanolic extract was evaporated to a pasty yellow solid which could be dissolved in a mixture of carbon tetrachloride, benzene and petroleum ether. On filtration a small amount of white solid, m.p. 161-171° was retained (material 'D'). Material 'D' was dissolved in hot petroleum ether and benzene. After crystallisation it weighed 2.97 g. and had a melting range (after drying) of 175-178°. The infrared spectrum showed it to be identical with trimethyl-(triphenylmethyl)-silane, with which it was combined. Hence the latter material must be slightly soluble in ethanol.

The remainder of the carbon tetrachloride-benzene-petroleum ether solution was evaporated yielding 61.73 g. orange pasty solid. Recrystallisation from petroleum ether gave a further 5.16 g. white crystalline solid, m.p. 160-170°; this was impure trimethyl-(triphenylmethyl)-silane.

Evaporation of the petroleum ether filtrate yielded an orange gum (33.58 g.) from which only traces of volatile material could be collected on distillation. Vacuum distillation

gave material 'C', a yellow oil (5.03 g.), b.p. 139-142°/0.25 mm., and left as residue a dark brown gum (material 'E'). Both showed similar infrared spectra. Neither gave a positive Beilstein's test for halogen but both contained silicon, as shown by the sodium peroxide fusion, ammonium molybdate-benzidine test.

In the refrigerator, material 'C' set to a glass, m.p. 53-59°. After crystallisation from benzene, 'C' crystallised as 1.41 g. efflorescent crystals, m.p. 72-79°. After vacuum drying 24.8% of the weight was lost [calculated for $(C_6H_5)_3CH \cdot C_6H_6$, 24.2%]. The dried material then melted at 89-91° (mixed melting point with triphenylmethane 91-94°). Hence material 'C' was identified as triphenylmethane. Evaporation of the mother liquors yielded a further material (0.87 g.), m.p. 84-89°. The total yield of triphenylmethane was 1.93 g. (4%).

The hard, gummy, undistilled material was dissolved in benzene. On partial evaporation, 3.51 g. material (apparently more triphenylmethane-benzene) was obtained making the total yield of triphenylmethane 4.63 g. (9.5%).

After removal of excess benzene in vacuo the residual material was a brown gum (17.71 g.) of the composition C, 84.76%; H, 7.52%; Si, 6.16%. This indicated the material to be a mixture.

Reaction of Diphenylmethylchlorosilane with
Sodium Triphenylmethyl

(1) To diphenylmethylchlorosilane (17.03 g., 0.073 mole) was added sodium triphenylmethyl in ether. Initially no precipitate was observed but after addition of a few ml. an orange precipitate was formed. This was filtered, leaving an orange waxy residue which became white on the surface on drying with the water aspirator. This material gave an intense sodium flame. The material sintered and darkened at 120-170° but did not melt. When treated with water a yellow solid was formed, m.p. 136-166°. On recrystallisation from benzene a very pale yellow solid melting at 171-173° and yielding a very dark orange liquid was obtained. The aqueous layer was strongly alkaline and contained halogen. The pale yellow solid was boiled with concentrated sulphuric acid and a drop of nitric acid. The liquid was decanted and the water poured into a tube. No gel was formed indicating the material to be silicon free¹¹⁵.

The ethereal filtrate deposited a white solid which was insoluble in water, m.p. 163-165°. This was crystallised from a benzene-chloroform solvent pair to m.p. 174-175.5°.

¹¹⁵H. Gilman and G.N.R. Smart, J. Org. Chem., 15, 720 (1950).

This was insoluble in concentrated hydrochloric acid, showing it not to be triphenylmethanol, but it dissolved in concentrated sulphuric acid with the formation of a very dark solution. On the addition of water, a light brown precipitate, m.p. 131-149° (dec.), was formed.

The ethereal solution reacted with sodium hydroxide precipitating a material which, when recrystallised from benzene, had a melting point of 43°. This was not depressed on admixture with an authentic sample of sym-tetraphenyldimethyldisiloxane. More precipitate was formed on allowing the filtrate to stand in air, showing much of the filtrate to be unreacted chlorosilane.

(11) To diphenylmethylchlorosilane (23.25 g., 0.1 mole) in ether (100 ml.) was added dropwise with stirring to 0.146 N sodium triphenylmethyl in ether (750 ml.). The reaction mixture was stirred for over 5 hours. Decolourisation occurred with the addition of the first 20 ml. of base, then the solution became yellow and finally red. Water (200 ml.) was added and the mixture was stirred for an additional 2 hours. The layers were separated.

The aqueous layer was not alkaline to litmus. On evaporation it afforded 7.32 g. white solid (theory, 5.85 g. sodium chloride). Gravimetric analysis showed 4.45 g. chloride, or more than theoretical.

The ethereal layer was dried over sodium sulphate then evaporated in vacuo. At this point the flask dropped into the water bath. The ethereal layer was separated, re-dried over sodium sulphate, and the ether was evaporated again. A clear brown gum (27.68 g.) was left which appeared to deposit a little solid on washing with 99% ethanol. It was extracted in a Soxhlet extractor with 300 ml. 99% ethanol but only a small amount dissolved. The yellow gum which remained did not crystallise after six days in the refrigerator. It was dissolved in benzene and ethanol was added until crystallisation occurred. After one month a gummy solid was filtered off but the material could not be induced to crystallise.

All microanalyses were done by the Schwarzkopf Microanalytical Laboratory, 56-19 37th Avenue, Woodside 77, New York, with the exception of two which were done by Spang Microanalytical Laboratory, P.O. Box 1111, Ann Arbor, Michigan.

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