SOME ORGANOPHOSPHORUS COMPOUNDS

CONTAINING SILICON

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By

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STATEMENT

The experimental work herein described
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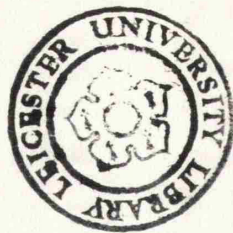not concurrently being presented, for any other
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. <u>Summary</u>

Reviews are given on the preparation and
properties of arylphosphorus compounds and aliphatic
phosphorus compounds containing silicon; on the cleavage
of the aryl-silicon bond in acid media; and on the
cleavage of the benzyl-silicon bond in alkaline media.

Detailed information has been obtained on the
effect of a variety of phosphorus-containing nuclear
substituents on the rates of cleavage of the aryl-
silicon bond in concentrated sulphuric acid-glacial
acetic acid, and of the benzyl-silicon bond in aqueous
methanolic-sodium hydroxide solution. The substituents
were found, in most cases, to be strongly electron-
withdrawing and the results clearly indicate that the
π-electrons of the benzene ring can enter the <u>d</u>-orbitals
of phosphorus.

The protonation, in strongly acidic media, of
the phosphoryl-oxygen, in triphenylphosphine oxide,
was studied spectrophotometrically. It is apparent
that triphenylphosphine oxide does not behave as a
true Hammett base.

Several silicon-substituted derivatives of

ethylphosphonic acid and dimethyl ethylphosphonate
were prepared and the properties of these investigated,
with special reference to pyrolytic and solvolytic
reactions.

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CHAPTER I

The Preparation and Properties of Aromatic Phosphorus

Compounds

The Preparation and Properties of Aromatic Phosphorus
Compounds

Aromatic phosphorus compounds have been
known since the 1890's. However, it is only during
the last fifteen years, when more sophisticated
techniques for their preparation have been
discovered, that aromatic phosphorus compounds have
become more widely studied.

The Nomenclature of Organophosphorus Compounds

Because of the difficulties in providing
unambiguous names for organophosphorus compounds
a standard system was adopted in 1952.[1] This
system uses, as parent structures, a number of
hydrides and oxyacids of phosphorus, some of which
are hypothetical. The parent structures most
frequently met with are: H_3P, phosphine; H_3PO,
phosphine oxide; $HPO(OH)_2$, phosphonic acid;
$H_2PO(OH)$, phosphinic acid; $PO(OH)_3$, phosphoric
acid.

When hydrogen, attached to phosphorus,
is replaced by an alkyl or aryl group the parent
compound has the name of the group prefixed to it

(e.g. Ph_3P, triphenylphosphine; $PhMe_2PO$, dimethyl-phenylphosphine oxide; $PhPO(OH)_2$, phenylphosphonic acid). Esters of phosphorus acids are named in the standard way (e.g. $PhPO(OEt)_2$, diethyl phenyl-phosphonate). For C-P containing acids, when a hydroxy group is replaced by halide, the compound takes the name of the acid followed by the name of the halide (e.g. $PhPOCl_2$, phenylphosphonic dichloride). Acid chlorides of phosphates are named in the following way: e.g. $(EtO)_2POCl$, diethylphosphorochloridate.

The Preparation of Aromatic Phosphorus Compounds

(a) Phosphonic acids and phosphonates

(i) Direct phosphonation of aromatic hydrocarbons

Phenylphosphonous dichloride may be prepared by passing the mixed vapours of benzene and phosphorus trichloride through a red-hot tube.[2]

$$PCl_3 + C_6H_6 \longrightarrow C_6H_5PCl_2 + HCl$$
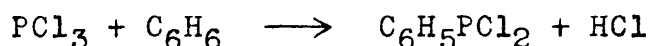
Reaction of phenylphosphonous dichloride with chlorine, in the presence of phosphorus pentoxide, leads to the formation of phenylphosphonic dichloride,[3] which may then be hydrolysed to phenylphosphonic acid.

The reaction is of little value with substituted aromatic hydrocarbons.

The Friedel-Crafts reaction between phosphorus trichloride and substituted aromatics, in the presence of aluminium chloride, has been used for nearly one hundred years for the production of arylphosphonous dichlorides.[4] The product is isolated from the reaction mixture by the addition of phosphorus oxychloride, to break down the complex between aluminium chloride and the chlorophosphine.[5] An alternative method of isolation, giving the phosphonic acid or phosphonate directly, has been developed by Kosolapoff.[6] The reaction mixture is treated with chlorine, followed by hydrolysis with water to give the phosphonic acid, or treated with an alcohol and distilled, to give the phosphonate.

The reaction has, however, a serious drawback in that the position of substition is uncertain, and in many cases, diverse. Thus Kosolapoff[7] has isolated, from the reaction of toluene with phosphorus trichloride, a mixture of o-tolyl, m-tolyl and p-tolyl-phosphonic acids, in the ratio 10:27:63 respectively.

The direct phosphonation of aromatic
hydrocarbons was first reported in 1954.[8] It was
found that benzene, chlorobenzene, o-xylene and
naphthalene could be phosphonated by heating with
phosphorus pentoxide at 275-325°. The phosphonic
acid was isolated by hydrolysis of the resultant
tar. Thus, by heating benzene (20 mole) and
phosphorus pentoxide (1 mole), the yield of phenyl-
phosphonic acid isolated was 75% of the theoretical.
Chlorobenzene gave mainly p-chlorophenylphosphonic
acid, although some of the ortho-isomer was isolated.

The first homolytic substitution of an
aromatic compound was reported by Jason and Fields
in 1960.[9] Thus, when a mixture of methyl benzoate
and diethyl phosphonate was treated with a molar
equivalent of di-t-butyl peroxide, an oil was
obtained, which, when hydrolysed with concentrated
hydrochloric acid, gave p-carbmethoxyphenylphos-
phonic acid, in 65% yield. The following mechanism
was suggested for the reaction:-

$$(Bu^tO)_2 \longrightarrow t\text{-}BuO\cdot$$

$$t\text{-}BuO\cdot + HPO(OEt)_2 \longrightarrow t\text{-}BuOH + \cdot PO(OEt)_2$$

COOMe

+   ·PO(OEt)$_2$ $\longrightarrow$

COOMe

—H

t-BuO·∕

H   ⟍PO(OEt)$_2$

COOMe

PO(OEt)$_2$
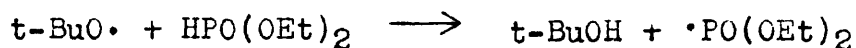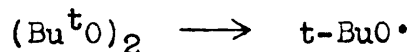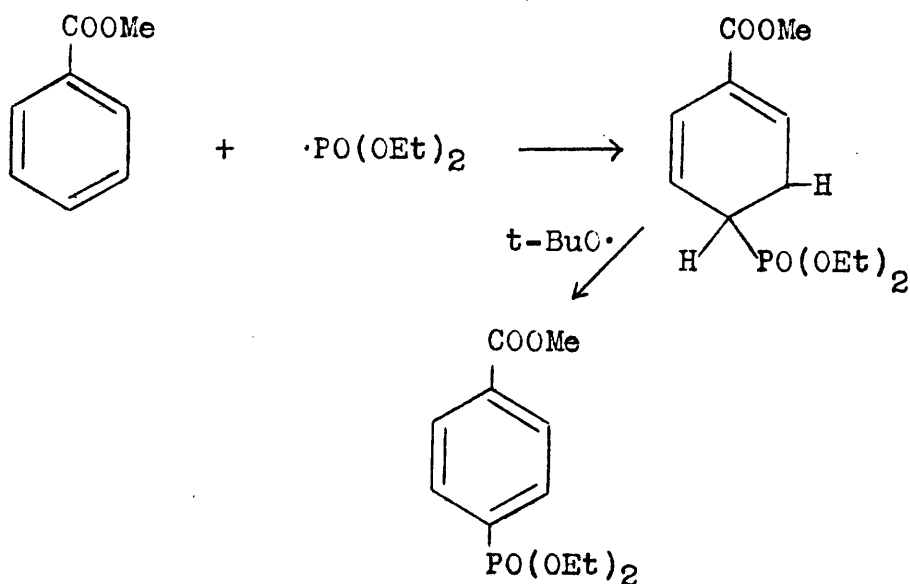
Subsequently, the same authors have described the successful phosphonation of the polycyclic aromatic hydrocarbons: naphthalene, anthracene, phenanthrene, dibenzfuran and carbazol.[10]

(ii) The reaction of diazonium salts with halides of tervalent phosphorus

A most useful general reaction for the preparation of arylphosphonic acids has been developed by Doak and Freedman.[11] It consists of adding phosphorus trichloride to an aryldiazonium fluoroborate in a dry solvent (dioxan or ethyl acetate), in the presence of cuprous chloride.

The reaction mixture is then treated with water and steam-distilled to remove the solvent.

$$Ar \cdot N_2^+ \ BF_4^- + PCl_3 \longrightarrow N_2 + Ar \cdot PCl_3^+ \ BF_4^-$$

$$\downarrow H_2O$$

$$ArPO(OH)_2$$
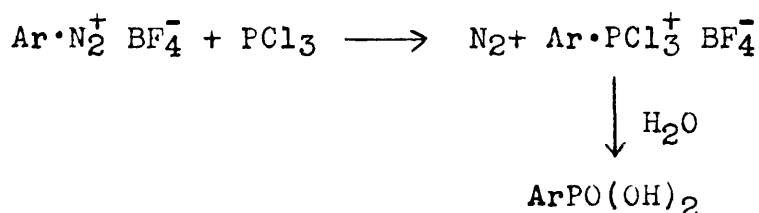
Although yields vary from 10-70%, depending on the substituted amine, the reaction is superior to those described above in that the orientation of the product is certain. A considerable quantity of diarylphosphinic acid is often obtained, presumably by the reactions:-

$$Ar \cdot PCl_3^+ \ BF_4^- + PCl_3 \longrightarrow Ar \cdot PCl_2 + PCl_4^+ \ BF_4^-$$

$$\downarrow Ar \cdot N_2^+ \ BF_4^-$$

$$Ar_2P(O) \cdot OH \xleftarrow{H_2O} Ar_2PCl_2^+ \ BF_4^- + N_2$$
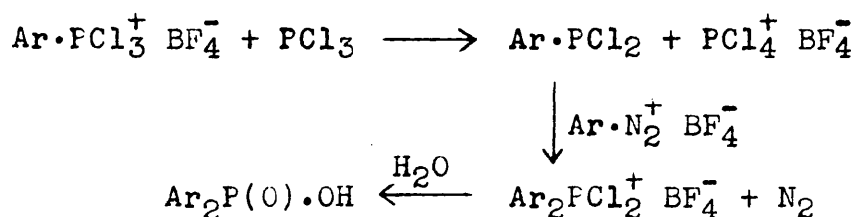
(iii) <u>The reaction of organometallic reagents with phosphonyl chloride and its derivatives</u>

The reaction of an aryl-lithium reagent with phosphonopiperidic chloride, and subsequent hydrolyses, gives a good yield of the arylphosphonic acid.[12]

e.g. $PhLi + (C_5H_{10}N)_2POCl \longrightarrow PhPO(NC_5H_{10})_2$

$$\downarrow HCl$$

$$PhPO(OH)_2$$
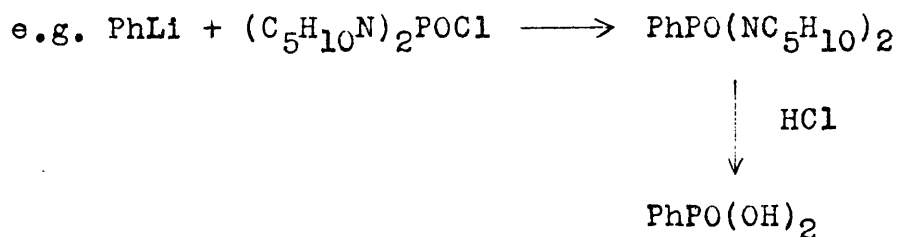
In 1951, Burger and Dawson showed that the addition of diethylphosphorochloridate to ortho-substituted aryl-Grignard reagents gave diethyl arylphosphonates, whereas sterically unhindered Grignard reagents gave triarylphosphine oxides.[13]

e.g. $\underline{o}-MeC_6H_4MgBr + (EtO)_2POCl \longrightarrow \underline{o}-MeC_6H_4PO(OEt)_2$
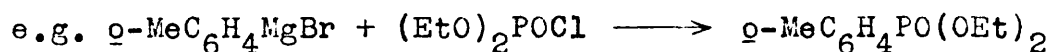
However, "reverse addition" of an unhindered reagent to diethylphosphorochloridate, gave the diethyl arylphosphonate in good yield.

e.g. $\underline{p}-CH_3C_6H_4MgBr + (EtO)_2POCl \longrightarrow \underline{p}-CH_3C_6H_4PO(OEt)_2$
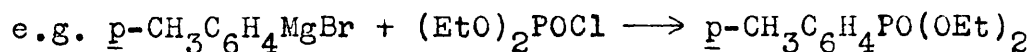
(b) Phosphine oxides

Arylphosphine oxides are best prepared by the reaction of arylmagnesium halides or aryl-lithium reagents with phosphoryl chloride, or substituted phosphonic dichlorides or phosphinic chlorides. The reaction usually gives good yield and the products are readily isolated.

Burger and Dawson[13] have investigated the reaction of arylmagnesium halides with diethyl-phosphorochloridate and have shown that it is possible to replace both chloro- and ethoxy- groups. Kosolapoff, however, has shown that diethyl phenyl-phosphonate will not react with phenylmagnesium bromide to give triphenylphosphine oxide.[14] This apparent anomaly has been explained by Burger and Dawson,[15] who found that for ethoxy- groups attached to phosphorus to be replaced, the presence of a magnesium halide is necessary. They postulate the following reaction series:

$$PhPO(OEt)_2 \xrightarrow{MgBr_2} Ph\overset{\overset{\displaystyle OMgBr_2}{|}}{P}(OEt)_2 \xrightarrow{PhMgBr} Ph_3PO$$
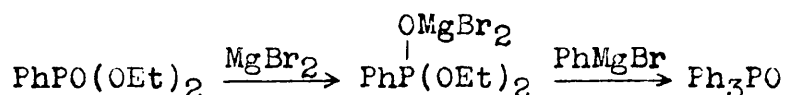
Thus, by coordination of phosphonyl groups with magnesium bromide, the phosphorus atom becomes more susceptable to nucleophilic attack.

It has since been shown that a Grignard reagent will react with diethyl phenylphosphonate, to give the phosphine oxide, when forcing conditions are used (i.e. a high-boiling solvent and an excess of the Grignard reagent).[16]

(c) Arylphosphates

When an excess of a phenol is heated with phosphoryl chloride, the corresponding triaryl phosphate is obtained in reasonable yield.

$$3ArOH + POCl_3 \longrightarrow (ArO)_3PO$$
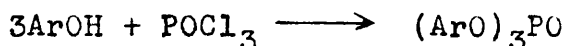
The reaction has been the subject of a number of patents in which it is claimed that reaction is facilitated by adding various reagents (e.g. magnesium chloride,[17] aluminium chloride,[18] and iodine [19]).

An alternative, and perhaps more suitable reaction for laboratory scale preparations, is the reaction of a sodium phenoxide with phosphoryl chloride in an inert solvent.[20,21]

$$3ArONa + POCl_3 \longrightarrow (ArO)_3PO + 3NaCl$$
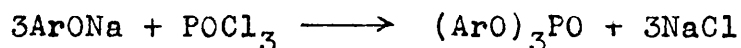
Canavan and Eaborn have successfully applied this method to the preparation of tris-(p-trimethylsilylphenyl)phosphate.[22] A modification of this method, using one mol. each of sodium p-trimethylsilylphenoxide and dimethylphosphorochloridate, gave dimethyl-p-trimethylsilylphenylphosphate.[23]

(d) Arylphosphonium salts

Trialkylarylphosphonium halides may be prepared simply by mixing a solution of the appropriate phosphine with an alkyl halide.[24]

$$PhPMe_2 + MeI \longrightarrow (PhPMe_3)^+ I^-$$
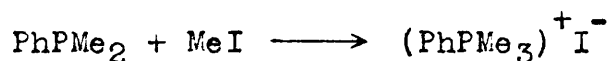
The reaction occurs much more readily than the quarternisation of the corresponding amine or arsine.[25]

Arylphosphines containing nuclear substituents show a marked substituent effect.[25] Thus, in the reaction of diethylarylphosphines with ethyl bromide, the reactivity of the arylphosphine decreases in the following way:

$$p-Et \rangle p-MeO \rangle p-CH_3 \rangle H \rangle p-Cl \rangle p-Br \rangle p-I \rangle$$
$$m-NO_2 \rangle p-NO_2$$
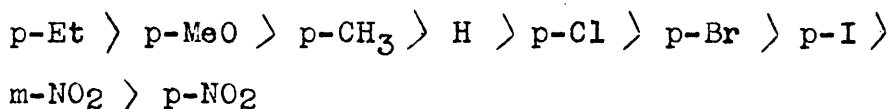
The reaction also shows a marked dependence on steric effects, as is demonstrated by the extremely slow rate of quarternisation of a substituted phosphine with neopentyl halides.[26]

Tetraphenylphosphonium compounds cannot be prepared by straightforward quarternisation.

Table I

Compound	Primary band λ_{max}	ϵ	Secondary band λ_{max}	ϵ
C_6H_6			254.5	180
$C_6H_5PO(OH)_2$			263.5	524
$C_6H_5PO_3H^-$			263.0	383
$C_6H_5PO_3^=$			258.0	239
$(C_6H_5)_2PO(OH)$	224	13,100	265.0	1,200
$(C_6H_5)_3PO$	224	21,300	265.0	2,420
$(C_6H_5)_3P$			261.0	11,000

The triarylphosphine and the aryl halide must be
heated with aluminium trichloride before reaction
will occur,[27] presumably via the phosphine/aluminium
trichloride adduct.

The Properties of Arylphosphorus Compounds

Absorption spectra

The ultraviolet spectra of a number of
arylphosphorus compounds have been recorded.[28,31]
In general, quadruply connected phosphorus causes
no large change in the general appearance of the
benzene spectrum. The absorption maxima is shifted
towards the visible by about 10 mμ and this shift
is usually accompanied by a slight increase in
intensity of absorption.

Jaffe and Freedman have determined the
ultraviolet spectra of some compounds containing
the phosphoryl bond (P=O) and their results are
given in Table I.[28]

Sklar[29] has pointed out that the spectra
of substituted aromatic compounds, in which
resonance can occur between the ring and the

substituent, differ markedly from the spectra of
the parent compounds, while purely inductive
substituents cause little change in λmax or
intensity. Thus, the relatively small effect of
the phosphono-group indicates that little resonance
interaction is occurring between the ring and the
vacant d-orbitals of phosphorus.

It has been shown that the difference
between the ultraviolet spectra of compounds of
the type Ph_2X and PhX is a measure of conjugation
between the phenyl groups in the former.[30] The.
absence of any marked difference in the spectra
of phenylphosphonic acid, diphenylphosphinic acid
and triphenylphosphine oxide (apart from the
increase in absorption due to the increasing number
of phenyl groups) implies that the phenyl groups
are not forming a conjugated system with the
central atom.

Included in Table I are the λmax and
extinction coefficient for triphenylphosphine.
Here the large intensification may be ascribed
to the interaction of the lone pair on phosphorus
with the π-electrons of the benzene ring.

-13-

Bowden and Braude[31] have examined the
effects of the groups; NMe_2, PMe_2, $AsMe_2$ and $SbMe_2$;
together with the corresponding quarternary iodides
(NMe_3^+; PMe_3^+; $AsMe_3^+$ and $SbMe_3^+$). With the trivalent
substituents a large bathochromic shift and
intensification, associated with the lone pair
interaction with the benzene ring, was observed.
The effect was greatest with the amine and decreased
down the series, presumably because of increasing
inertness of the lone pair. The quarternary "onium"
iodides showed, in the π-π^* region at least
(absorption below 255 mμ was masked by the strong
iodide absorption), very little difference in
spectra from that of benzene. The bathochromic
shift decreased from between <u>ca</u>. 15-2 mμ in the
following order:

$$PMe_3^+ \rangle \; AsMe_3^+ \rangle \; SbMe_3^+ \rangle \; NMe_3^+.$$
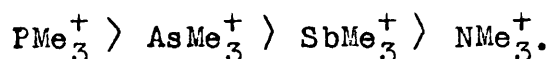
The slight increase in intensity, compared with
that of benzene, varied similarly.

Thus, it appears that there is only weak
resonance interaction between the vacant phosphorus
d-orbitals and the π-electrons of the benzene ring.

It has been proposed, however, that $d\pi-p\pi$ bonding
might occur between phosphorus and aromatic systems
if a strong electron donor is present in the
aromatic system.[32] This was confirmed by Griffin
and Polsky,[33] who found that tri-2-pyrylphosphine
oxide has an intense band at 237.5 mμ (log ϵ, 4.06),
which is absent in pyrol. This has been interpreted
as evidence for strong $d\pi-p\pi$ bonding between the
aromatic ring and the phosphorus atom.

The cleavage of the aryl-phosphorus bond

The aryl-phosphorus bond displays a high
order of chemical and thermal stability, as is
confirmed by the C-P bond energy of 62 kcal.
(cf. C-C, 64 kcal.).[34] Circumstances in which
phosphorus is cleaved from an aromatic nucleus are
remarkably few and quite drastic conditions are
required. Thus, the cleavage of a phenyl group
from triphenylphosphine oxide occurs when this is
fused with sodium hydroxide at 250-230°.[35]

$$Ph_3PO + NaOH \longrightarrow C_6H_6 + Ph_2P(O)ONa$$
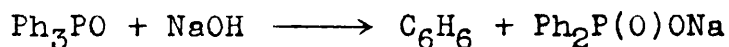
Further cleavage does not take place and the
sodium salt of diphenylphosphinic acid is isolated

in high yield.

In most cases the aryl-phosphorus bond
can withstand treatment by strong acids. Phenyl-
phosphonic acid and triphenylphosphine oxide have
both been nitrated in fuming nitric acid and
dialkyl arylphosphonates can be successfully
hydrolysed using concentrated hydrochloric acid
at reflux temperature. However, the presence of
a strongly electron-donating substituent, ortho
or para to the aryl-phosphorus bond, causes a
marked decrease in its stability to electrophilic
reagents.

The instability of p-dimethylaminophenyl-
phosphonic acid was noted by Michaelis and Schenk
in 1888.[36] They observed that the compound was
decomposed to dimethylaniline and phosphoric acid
by warming its aqueous solution and that the reaction
occurred much more quickly in acid solution.

Subsequently other such cleavage reactions
have been observed. p-Methoxyphenylphosphonic acid
was cleaved to anisole and phosphoric acid by 66%
hydrobromic acid,[37] and 2-methoxy-4-nitrophenyl-

phosphonic acid was cleaved by 48% hydrochloric acid.[38]

The cleavage of p-methoxyphenylphosphonic acid has been studied kinetically and shown to be first order in phosphonic acid but more complex in hydrogen ion concentration.[39] The reaction was studied spectrophotometrically, using sulphuric acid of various concentrations (9-60%). Over the acid concentration range 9-30% the rate of cleavage was shown to increase rapidly, with increase in acid concentration, but as the acid concentration approached 60% the rate of increase in rate became slower. No explanation has been proposed for this behaviour.

Electrophilic substitution in arylphosphorus compounds

Arylphosphonic acids and arylphosphonates

For many years, nitration of phenyl-phosphonic acid was thought to give m-nitrophenyl-phosphonic acid exclusively.[40,41] However, in 1955 Doak and Freedman detected 13% of the ortho-isomer in a reaction mixture which gave mainly m-nitro-phenylphosphonic acid.[42] Similarly, nitration of diethyl phenylphosphonate was found to give mainly

diethyl m-nitrophenylphosphonate, together with a small amount of the ortho-isomer.[43] The reaction appears to proceed more slowly than the nitration of dibutyl benzylphosphonate,[44] which nitrates to give the para-isomer exclusively, diethyl phenylphosphonate requiring slightly elevated temperatures, while the benzylphosphonate reacts in the cold.

These observations show that the dihydroxyphosphonyl and diethoxyphosphonyl substituents are electron-withdrawing. Further, the isolation of the ortho-isomer as a by-product indicates that the substituent is conjugated with the ring, since with purely inductively withdrawing substituents the ortho is deactivated more strongly than the para-position.[45]

Reports of nitrations of 2,4- and 2,5-dimethylphenylphosphonic acid,[46] o- and p-tolylphosphonic acid,[47] p-bromophenylphosphonic acid[48] and p-chlorophenylphosphonic acid[49] have appeared in the literature. In each case it is assumed that the nitro-group goes completely into the position meta to the phosphorus group.

Jaffe, Doak and Freedman[50] have obtained
σ-constants for $\underline{m}$- and $\underline{p}$-PO_3H^- and $\underline{m}$- and $\underline{p}$-$PO_3^=$
(Table II).

Table II. Substituent constants for phosphono-anions

Substituent	σ_m	σ_p
PO_3H^-	0.25^a, 0.24^b	0.17^a, 0.29^b
$PO_3^=$	-0.02^c	-0.16^c

(a) From the ionisation constant of the -COOH
     group in water.

(b) From the ionisation constant of the -COOH
     group in aqueous ethanol (50%).

(c) From the ionisation constant of phenolic
     -OH in water.

Their results can be considered as only
rough estimates of the substituent constants.
However, it may be concluded that the $-PO_3H^-$
group is weakly electron-attracting from both the
meta and para positions and that the $-PO_3^=$ group
is electron-repelling from both positions.

It has been suggested that, for a given
position, a single σ-constant should be applicable
to the free carboxy and the carbethoxy substituents,[51]

and it is logical to assume that similar reasoning
may be applied to the $-PO(OH)_2$ and $-PO(OEt)_2$
substituents. Jaffe and Freedman determined the
σ-constants for m- and for p-PO(OEt)$_2$, by measurement
of the ionisation constants of a number of suitably
substituted acids.[52] Table III summarises their
results.

Table III. Substituent constants for the diethoxy-
            phosphono-group

R $\left[\text{in } (EtO)_2OPC_6H_4R\right]$	pK_a	σ	ρ
p-COOH	3.60	0.60	1.000
p-NH$_3^+$	2.22	0.84	2.767
p-OH	8.28	0.73	2.113
m-COOH	3.65	0.55	1.000
m-NH$_3^+$	3.09	0.53	2.767
m-OH	8.66	0.56	2.113

The value for σ_m is constant within the
limits of the method and the mean value of 0.55
has been assigned to it. However, σ_p varies,
depending on the reaction, and belongs to the class

of substituents requiring an exalted σ-constant (σ^-) for reactions in which direct resonance can occur between the substituent and the reaction site.[51]

Phosphine oxides

The nitration of triphenylphosphine oxide,[53] butyldiphenylphosphine oxide[54] and bis-(chloromethyl)phenylphosphine oxide[55] have been reported and in each case the meta-isomer only was isolated. The results suggest that the phosphoryl function is a strongly electron-attracting group, similar to the carbonyl group.

When tribenzylphosphine oxide was nitrated the para-isomer was isolated in good yield but it probably contained a trace of the ortho-isomer.[56]

Phosphates

The nitration of a number of arylphosphates indicates that the -O.PO(OR)$_2$ group (R = alkyl or aryl) is o/p-directing. Thus, the nitration of diethylphenylphosphate, with fuming nitric acid, at $0°$, gave a mixture of its ortho-and para-nitro

derivatives.[57,58] Triphenylphosphate, when nitrated in fuming nitric acid, at $0°$, gave a mixture of tris-(o-nitrophenyl)phosphate and tris-(p-nitrophenyl)phosphate.[59] Nitration in mixed acid, at $80°$, gave tris-(2,4-dinitrophenyl)phosphate.[60]

Arylphosphonium salts

A comparative study of the nitration of the group V phenyl, and benzyl "onium" picrates, was made by Ingold, Shaw and Wilson[61] (Table IV).

Table IV. The percentage of m-substitution in the nitration of phenyl and benzyl "onium" picrates

Substituent	Phenyl % m-NO$_2$	Benzyl % m-NO$_2$
-NMe$_3^+$	100%	88%
-PMe$_3^+$	100%	10%
-AsMe$_3^+$	98%	4%
-SbMe$_3^+$	86%	-

The positively charged substituents show a strong m-orienting effect which falls off as the periodic group is descended. This phenomena is particularly noticeable in the benzyl derivatives.

Ingold explained this fall-off in terms of decreasing electronegativity of the central atom, and also increasing shielding of the nucleus by surrounding electrons.

The Phosphoryl Bond

The exact nature of the phosphoryl bond in compounds of the type R_3PO was for a long time a matter of controversy, since it can be represented as a double covalent bond, $R_3P=O$, requiring expansion of the phosphorus octet or alternatively, in accordance with the octet theory, as a semi-polar bond, $R_3\overset{+}{P}-\overset{-}{O}$. It is now generally accepted that the phosphoryl bond is semi-polar, but modified by some back coordination from the filled 2p-orbitals of the oxygen atom.[62]

The extent of the π-bonding is very much dependant on the nature of the attached groups (R), as is indicated by the large variation in the phosphoryl stretching frequency (1210-1430 cm.$^{-1}$) observed in a wide range of variously substituted phosphoryl compounds. (A variation in stretching frequency (ν) represents a change in force constant, which implies a change in bond orders.) Substituents

which are strongly electron-withdrawing cause an increase of ν, while with electron-repelling groups the reverse obtains. Bell et al.[63] have shown that there is an excellent correlation between the wavelength of the phosphoryl absorption and the electronegativities of the attached groups. More recently, molecular orbital calculations have shown that the phosphoryl bond varies from an almost pure single bond in Me_3PO to nearly a triple bond in F_3PO.[64] The calculated π-bond orders for a number of compounds gave a straight line correlation with observed stretching frequencies.

The observed dipolar character of the phosphoryl bond arises mainly as a result of contribution from the semi-polar structure, $\equiv\overset{+}{P}-\overset{-}{O}$, and also because the main region of overlap in the $d\pi$-$p\pi$ bond is in the vicinity of the oxygen atom.[65]

The high polarity of phosphoryl compounds manifests itself in a number of chemical properties. Thus, trialkylphosphine oxides are extremely hygroscopic.[66] Triphenylphosphine oxide has been shown to form hydroxyphosphonium salts with strong

acids; the nitrate, $Ph_3\overset{+}{P}OH$ NO_3^-[67] and the hydro-chloride, $Ph_3\overset{+}{P}OH$ Cl^-[68] have been characterised. The donor properties of the phosphoryl oxygen in triphenylphosphine oxide are well-known, and a number of complexes with compounds such as stannic chloride,[69] antimony pentachloride[70] and the interhalogens[71] have been isolated.

CHAPTER II

The Cleavage of the Aryl-silicon Bond in Acid Media

The Cleavage of the Aryl-silicon Bond in Acid Media

The first report of the aryl-silicon bond was made by Kipping and Lloyd,[72] who observed that tetraphenylsilane was slowly decomposed in glacial acetic acid, at $130°$:

$$Ph_4Si + H_2O \xrightarrow{H^+} Ph_3SiOH + C_6H_6$$
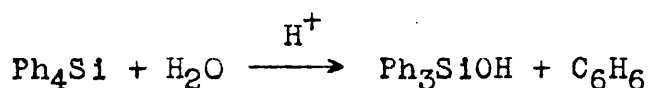
Gilman and Marshall[73] studied the cleavage of a number of substituted aryltrimethylsilanes by passing dry hydrogen chloride through a solution of the silane in refluxing glacial acetic acid. The trimethylchlorosilane evolved was collected in a cold-trap, and the rate of its formation was taken as a measure of the ease of cleavage. The following series of relative reactivity was obtained:

2-thienyl $\rangle$ p-methoxyphenyl and p-dimethylaminophenyl$\rangle$ p-tolyl $\rangle$ phenyl $\rangle$ p-chlorophenyl $\rangle\rangle$ benzyl

The reaction was also studied by Benkeser and Krysiak[74] in this way, and they established the following series of reactivity:

p-MeO and p-NMe$_2$ $\rangle$ p-CH$_3$ $\rangle$ m-MeO $\rangle$ m-CH$_3$ $\rangle$ H $\rangle$ p-Cl
m-Cl $\rangle$ m-NMe$_2$

Subsequently, an extensive study of the acid cleavage of the trimethylsilyl group, from a wide range of substituted aryltrimethylsilanes, has been made by Eaborn and his coworkers. It was shown that the reaction could be readily studied spectrophotometrically, since the presence of a trimethylsilyl group shifts the ultraviolet benzene spectrum 2-15 mμ towards the visible, and also causes an intensification of absorption.

The results of a preliminary investigation on p-methoxyphenyltrimethylsilane, in methanol-perchloric acid and in hydrochloric acid, showed that the reaction was first order in silane.[75] The rate of cleavage was also shown to exhibit a linear dependence on the acidity function, H_0 (i.e. a measure of the ability of a medium to donate a proton to a neutral base). Such a linear dependence is thought to indicate that a fast, reversible proton transfer, from solvent to reactant, is taking place before the rate-determining step.[76,77] The reaction mechanism proposed was:

$$\underline{p}\text{-}Me_3SiC_6H_4OMe + H^+ \overset{fast}{\rightleftharpoons} \underline{p}\text{-}Me_3SiC_6H_5OMe^+$$

(I)
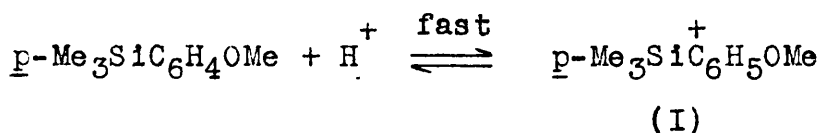
Table V. The cleavage of substituted phenyltrimethyl-
silanes.

Substituent	k_{rel} (HClO$_4$-MeOH-H$_2$O)	k_{rel} (H$_2$SO$_4$-CH$_3$COOH-H$_2$O)
p-NMe$_2$	c.a. 3.0 x 10^7	
p-OH	10,700	
p-OMe	1,510	1,110
p-Me$_3$SiCH$_2$	315	200
p-Me	21	
p-Et	19.5	
p-Pr^i	17.2	
p-Bu^t	15.6	
m-Me$_3$SiCH$_2$	6.2	
p-Ph	3.5	2.8
m-Me	2.3	
p-Me$_3$Si	1.25	
H	1.0	1.0
p-F	0.75	0.95
m-OMe		0.38
m-Ph		0.33
p-Cl	0.13	0.19
p-Br	0.10	0.10
p-I		0.10

Table V (continued)

Substituent	k_{rel} (HClO$_4$-MeOH-H$_2$O)	k_{rel} (H$_2$SO$_4$-CH$_3$COOH-H$_2$O)
m-Cl		0.012
m-COOMe		0.0111
m-COOH		0.0578
p-COOMe		0.00208
m-CF$_3$		0.00206
m-SO$_3$H		0.00159
p-COOH		0.00140
p-SO$_3$H		0.00099
p-NMe$_3^+$		0.00040
m-NO$_2$		0.00028
p-NO$_2$		0.00012

$$p\text{-}Me_3Si\overset{+}{C}_6H_5OMe + HOH \xrightarrow{\text{slow}} Me_3Si\overset{+}{O}H_2 + C_6H_5OMe$$

$$Me_3\overset{+}{Si}OH_2 \xrightarrow{\text{fast}} Me_3SiOH + \overset{+}{H}$$
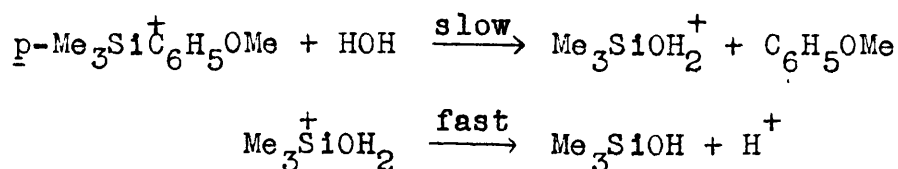
The reaction intermediate (I) is thought to be similar to those postulated for other electrophilic aromatic substitution reactions:[78]
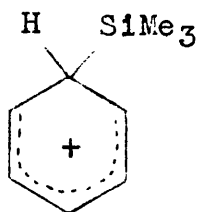
Further cleavage studies (in MeOH-HClO$_4$[79,80] and in CH$_3$COOH-H$_2$O-H$_2$SO$_4$[80,81]) on a wide range of substituted aryltrimethylsilanes showed that the reaction follows the usual pattern of electrophilic aromatic substitution, electron-supplying substituents facilitating it, and electron-withdrawing substituents retarding it.

Table V shows the effect of nuclear substituents on the rate of cleavage of a trimethylsilyl-group from substituted aryltrimethylsilanes.

The relative rate constants (k_{rel}) obtained correlate well with other electrophilic aromatic substitution reactions.[82] A plot of log k_{rel} versus

σ^+ (the substituent constant of Brown[83]) give points

lying well about a straight line. A better plot is

obtained if the relationship of Yukawa and Tsuno[84]

is used, where log k_{rel} is plotted versus $\sigma + r(\sigma^+ - \sigma)$:

where r is the parameter introduced to account for

the variation in electron demand on resonance effects

from reaction to reaction.($r = 0.67$ for protodesilylation).

Thus, the reaction provides a useful

measure of the effect of nuclear substituents in

electrophilic aromatic substitution, in a way far

superior to the usual substitution reactions studied

(e.g. nitration, chlorination, etc.) since the

position of attack is certain.

CHAPTER III

The Cleavage of the Benzyl-silicon Bond in Alkaline Media

The Cleavage of the Benzyl-silicon Bond in Alkaline
Media

The cleavage of the benzyl-silicon bond
in trialkyl- or triaryl-benzylsilanes, giving the
corresponding tolyl derivatives and hexa-alkyl-
or hexa-aryl-disiloxanes, has been demonstrated by
a number of workers.[85,86,87]

$$R_3SiCH_2C_6H_4X + HOH \xrightarrow{OH^-} CH_3C_6H_4X + R_3SiOH$$

$$2R_3SiOH \longrightarrow R_3SiOSiR_3 + H_2O$$
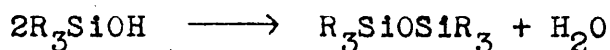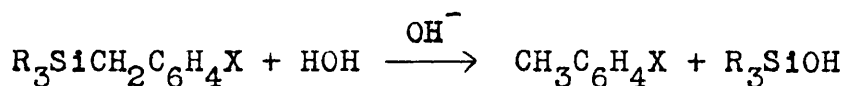
The first kinetic study of the cleavages,
of a number of substituted benzyltrimethylsilanes,
was made by Eaborn and Parker.[88] The reaction was
carried out in aqueous methanol (39 wt.% and 5 wt.%)
and was followed spectrophotometrically. The
cleavage proved to be first order in silane and it
was also found that the specific rate constant
($k_s = k_1/[NaOH]$) was independent of the alkali
concentration, at least for uncharged substituents.

The results indicate a marked dependence
on substituent effects, the reaction being
facilitated by electron-withdrawal. When log k_s

Table VI. The cleavage of substituted benzyltrimethyl-
silanes in 39 wt.% aqueous methanol

Substituent	k_{rel}	Substituent	k_{rel}
p-NO$_2$	18×10^5	m-Br	63
o-NO$_2$	50×10^4	m-Cl	63
p-COPh	15×10^4	o-SO$_3^-$	40
p-SO$_2$Ph	14×10^4	m-F	37
p-COCH$_3$	10×10^4	m-SO$_3^-$	35
p-CONHPh	70×10^2	p-I	35
p-CONH$_2$	63×10^3	m-CONHPh	31
p-SO$_3^-$	62×10	p-Br	19
o-CONH$_2$	53×10	o-F	15
p-CO$_2^-$	32×10	p-Cl	14
o-I	13×10	p-Me$_3$Si	9.6
m-CF$_3$	94	o-CO$_2^-$	4.8
o-Br	92	m-CO$_2^-$	2.1
o-Cl	80	H	1
m-I	65	p-MeO	ca. 0.02

was plotted against σ (the Hammett substituent

constant) an excellent straight line, of slope 4.88,

was obtained.[89] However, the p-NO$_2$ substituent

requires use of the σ^- constant for the point to

lie on the line. (The σ^- constant is used when

there is direct resonance interaction between

substituent and reaction site (e.g. in the ionisation

of phenols).[51]

The range of substituted benzyltrimethyl-

silanes studied, has been extended by Allcock[90] and

later by Rushton.[91] The results of all of these

studies are summarised in table VI.

The mechanism which Parker and Eaborn[88]

suggest for the reaction is one of the synchronous

bimolecular (S_N2) type:

$$YO^- + Me_3SiCH_2C_6H_4X \longrightarrow \overset{\delta-}{YO}\cdots SiMe_3\cdots \overset{\delta-}{CH_2}C_6H_4X$$

$$\downarrow$$

$$YOSiMe_3 + \bar{C}H_2C_6H_4X$$

$$\bar{C}H_2C_6H_4Y + HOY \longrightarrow CH_3C_6H_4X + OY^-$$

$$(OY^- = OH^- \text{ or } OMe^-)$$
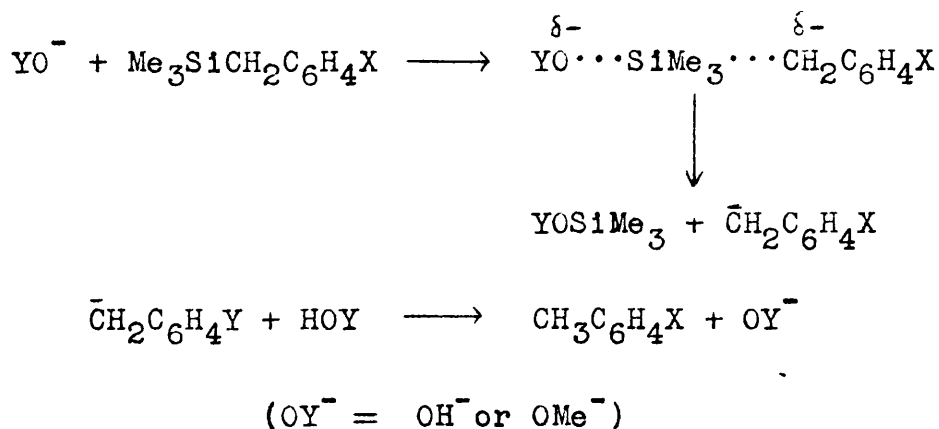
Electron withdrawal in the substituent facilitates

the reaction by allowing the nucleophile to approach
more readily, and also increases the ease of
separation of the benzyl group with the electrons
of the carbon-silicon bond. This explains the
outstanding effect of the p-NO$_2$ substituent, which
can stabilize the separating anion by inductive
withdrawal and also by resonance:
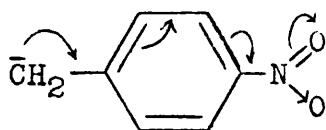
It was found that in aqueous methanol
solution the rate of cleavage increased with
increasing water concentration in the medium.
This observation is inconsistant with the proposed
mechanism, which involves a dispersion of charge.[92]
However, Eaborn and Parker[88] rationalise this
apparent anomaly by suggesting that the equilibrium,

$$H_2O + MeO^- \rightleftharpoons MeOH + HO^-$$
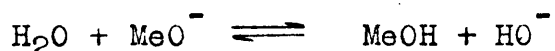
is moved further to the right when the water content
of the medium is increased, and that OH$^-$ ions have
a greater nucleophilic activity towards silicon
than have MeO$^-$ ions.

Although the first order specific rate
constant was found to be independent of the alkali
concentration for most of the compounds studied;
for the anions $Me_3SiCH_2C_6H_4CO_2^-$ it increased markedly
with increase in alkali concentration.[88] This rise
was attributed to the effect of an increase in
ionic strength of the medium. It was shown that
the addition of sodium chloride to the reaction
also caused an increase in specific rate constant,
indicating that this assumption is correct.[93]

CHAPTER IV

Discussion of Experimental Results

Discussion of Experimental Results

1. Preparative Methods

(a) Silicon-substituted phenylphosphonic acids and phenylphosphonates

The preparation of structures of the type $Me_3SiC_6H_4P(O)(OR)_2$, (R = H or Et) is complicated by the fact that the aryl-silicon bond is easily cleaved by electrophilic reagents. This precludes the use of the Friedel-Crafts reaction between phenyltrimethylsilane and phosphorus trichloride, to give a trimethylsilyl-substituted phenylphosphonous dichloride (which could then be converted to either the corresponding phosphonic acid or phosphonate), since the aluminium chloride catalyst would cleave off the trimethylsilyl-group. Similarly, m- and p-trimethylsilylphenylphosphonic acids could not be prepared by the method of Doak and Freedman;[11] (the reaction of aryldiazonium fluoroborates with phosphorus trichloride), as the silicon-aryl bond would certainly be cleaved at the diazotisation stage.

An attempted homolytic phosphonation of

phenyltrimethylsilane, with dimethylphosphonate, using di-t-butyl peroxide as catalyst, according to the method described by Jason and Fields,[9] gave a very low yield of a compound, the infrared spectrum of which was consistant with its being dimethyl p-trimethylsilylphenylphosphonate. Hydrolysis of this compound with concentrated hydrochloric acid, gave phenylphosphonic acid. The remainder of the products from the reaction mixture consisted of an unidentified, low-boiling silicon-containing compound, together with a large amount of a polymeric resin. The failure of the reaction to produce the desired product in high yield was probably due to the homolytic cleavage of the aryl-silicon bond. The low yield was not expected in the light of the observations of Rondesvedt and Blanchard,[94] who report the successful phenylation of phenyltrimethylsilane, using benzoyl peroxide (see also ref. 95, p.388).

Diethyl p-trimethylsilylphenylphosphonate was prepared by the "reverse addition" of the Grignard reagent from p-chlorophenyltrimethylsilane, to a cooled solution of diethylphosphorochloridate:

$$p\text{-Me}_3\text{SiC}_6\text{H}_4\text{MgCl} + (\text{EtO})_2\text{POCl} \longrightarrow p\text{-Me}_3\text{SiC}_6\text{H}_4\text{P(O)(OEt)}_2$$

$$(60\%)$$
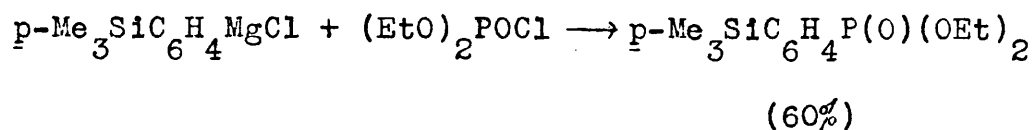
The meta-compound was prepared similarly, also in 60% yield.

Because of the convenience of this method it was used in the preparation of the corresponding benzyl-compounds, diethyl p-trimethylsilylmethyl-phenylphosphonate and diethyl m-trimethylsilyl-methylphenylphosphonate; these were obtained in 36% and 56% yield respectively.

The phosphonic acids, m- and p-$\text{Me}_3\text{SiC}_6\text{H}_4\text{P(O)(OH)}_2$ could not be prepared from the esters by the usual treatment with refluxing concentrated hydrochloric acid, since the trimethyl-silyl group would certainly be cleaved under the conditions of the reaction. It was found, however, that these acids were readily obtainable, by first converting the phosphonates to the corresponding phosphonic dichlorides, m- and p-$\text{Me}_3\text{SiC}_6\text{H}_4\text{POCl}_2$ (by refluxing the esters with phosphorus penta-chloride), which were then readily hydrolysable to the acids, using dilute aqueous sodium hydroxide

solution. The corresponding trimethylsilylmethyl-
substituted compounds were similarly obtained.

(b) Silicon-substituted tertiary phosphine oxides

The silicon-substituted phosphine oxides,
m- and p-$RC_6H_4P(O)R'_2$, (R = Me_3Si- and Me_3SiCH_2-;
R' = Me and Ph), were prepared by the reaction of
the phosphonic dichlorides, $RC_6H_4POCl_2$, with either
phenylmagnesium bromide or methylmagnesium iodide.
It is interesting to note that in each case the
meta-isomer could not be crystallised and had to
be purified by distillation at reduced pressure.
The para-compuonds all had melting-points greater
than 90°.

(c) Silicon-substituted aryl-phosphates

Diethyl-p-trimethylsilylphenylphosphate
was prepared by reacting diethylphosphorochloridate
with sodium p-trimethylsilylphenoxide:

$$p\text{-}Me_3SiC_6H_4ONa + (EtO)_2POCl \longrightarrow p\text{-}Me_3SiC_6H_4OP(O)(OEt)_2$$

$$(45\%)$$
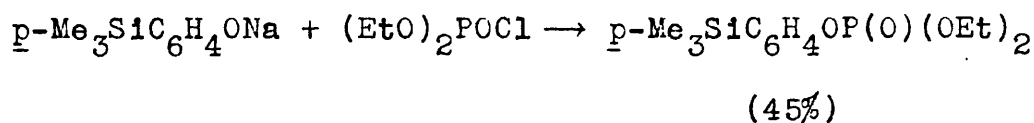
The corresponding meta-isomer was similarly prepared
and was isolated in 50% yield.

(d) Silicon-substituted arylphosphonium iodides

The phosphines, $RC_6H_4PMe_2$ ($R = Me_3Si$ or Me_3SiCH_2), were prepared by reducing the corresponding phosphine oxides, with lithium aluminium hydride, according to the method of Horner and Hoffman.[96] In each case no attempt was made to isolate the phosphine in a pure state, but it was immediately dissolved in benzene and excess methyl iodide added. The quarternisation reaction was in all cases instantaneous and the phosphonium iodides, $[RC_6H_4PMe_3^+] I^-$ were isolated in high yield. Trimethyl-p-trimethylsilylphenylphosphonium iodide was converted to the corresponding hydroxide, by boiling with silver oxide in aqueous solution. A similar attempt to prepare the corresponding meta-phosphonium hydroxide led to complete loss of the starting material and none of the desired product was isolated.

Table VII. Cleavage of phosphorus-substituted phenyl-
trimethylsilanes $(RC_6H_4SiMe_3)$

Substituent (R)	Acid ($\underline{M}$)	$\underline{k}_1$ (10^{-3}min.$^{-1}$)	$\underline{k}_{rel}$
$\underline{p}$-P(O)Ph$_2$	18.4	6.35	0.0000405
$\underline{p}$-P(O)Me$_2$	18.4	9.44	0.0000602
$\underline{p}$-PMe$_3^+$	18.4	11.03	0.0000710
$\underline{p}$-NO$_2$	18.4	13.8	
$\underline{p}$-P(O)(OEt)$_2$	18.4	18.4	0.000117
$\underline{p}$-P(O)(OH)$_2$	18.4	33.0	0.000211
$\underline{p}$-NMe$_3^+$	18.4	33.2	0.000212
$\underline{m}$-P(O)Ph$_2$	18.4	44.0	0.000271
$\underline{m}$-P(O)(OEt)$_2$	18.4	90.0	0.000574
$\underline{m}$-P(O)(OH)$_2$	18.4	151.0	0.000963
$\underline{p}$-NO$_2$	16.3	2.88	0.000088
$\underline{m}$-P(O)(OEt)$_2$	16.3	32.7	0.000994
$\underline{m}$-P(O)(OH)$_2$	16.3	43.9	0.00132
$\underline{m}$-CF$_3$	16.3	83.6	
$\underline{m}$-CF$_3$	11.7	1.75	0.00245
$\underline{m}$-O-P(O)(OEt)$_2$	11.7	7.96	0.0109
$\underline{m}$-Cl	11.7	9.68	
$\underline{m}$-Cl	9.9	2.45	0.0141
$\underline{m}$-CH$_2$P(O)(OEt)$_2$	9.9	36.6	0.211

Table VII. (continued)

Substituent (R)	Acid ($\underline{M}$)	$\underline{k}_1$ (10^{-3}min.^{-1})	$\underline{k}_{rel}$
$\underline{m}$-$CH_2P(O)(OH)_2$	9.9	54.7	0.315
$\underline{p}$-O-$P(O)(OEt)_2$	9.9	61.4	0.353
$\underline{p}$-$CH_2P(O)(OEt)_2$	9.9	121.2	0.695
$\underline{p}$-$CH_2P(O)(OH)_2$	9.9	134.1	0.771
H	9.9	173.4	1.00

2. The Acid Cleavage of some Phosphorus-substituted Phenyltrimethylsilanes

It is known that a quantitative measure of the effects of nuclear substituents in aromatic electrophilic substitution may be obtained by determination of the rate of acid cleavage of the aryl-silicon bond in substituted phenyltrimethyl-silanes.[79] This technique has now been used to determine the influence of various phosphorus-containing substituents in such reactions.

The results of this study are summarised in table VII. Certain non-phosphorus substituents were included for comparison and for use as "overlap" compounds so that relative rates may be obtained despite the fact that four different acid concentrations were used. Thus, the k_{rel} obtained for m-Cl in $9.9\underline{M}$ sulphuric acid was used to calculate relative rates for all compounds cleaved in $11.3\underline{M}$ sulphuric acid. Similarly, the figures for m-CF$_3$ and p-NO$_2$ were used for compounds cleaved in $16.3\underline{M}$ and $18.4\underline{M}$ sulphuric acid solutions respectively. (It should be noted that the quoted sulphuric acid molarity refers to the concentration of the added aqueous sulphuric acid

and not to the final concentration in the reaction

mixture.)

An examination of substituent effects

(a) Trimethylphosphonium group

The $-PMe_3^+$ substituent proved to be strongly

electron-withdrawing from the para-position, deactiv-

ating it approximately 1.25 times more than does the

$p-NO_2$ substituent. Unfortunately, the figure for the

$m-PMe_3^+$ group is not available as trimethyl-m-trimethyl-

silylphenylphosphonium hydroxide could not be prepared

from the corresponding iodide. (It was found necessary

to use the phosphonium hydroxides in this study, since

the iodides, in strong acid solution, liberated iodine

and also gave solutions which absorbed strongly in the

region of the ultraviolet spectrum at which the

reaction was followed.)

Nitration studies by Ingold, Shaw and

Wilson[61] indicated that the $-PMe_3^+$ substituent was

strongly deactivating and meta-directing. Their

results also indicated that the $-NMe_3^+$ substituent

exerts a far stronger electron-withdrawal than the

$-PMe_3^+$ substituent because, although the nitrations

of trimethylphenylammonium picrate and trimethyl-
phenylphosphonium picrate both led to the isolation
of 100% meta-isomer, the corresponding benzyl
compounds, trimethylbenzylammonium picrate and
trimethylbenzylphosphonium picrate, gave 88% meta-
isomer and 10% meta-isomer respectively, (see table IV,
p.21). Ingold explains this fall-off in -I effect in
terms of the lower "intrinsic electronegativity" of
phosphorus, and an increased screening of the nucleus
by its sub-valence shell electrons.

In protodesililylation the results show that
$-PMe_3^+$ is more deactivating than $-NMe_3^+$ from the para-
position by a factor of 3. This extra electron-
withdrawal is certainly associated with $d\pi-p\pi$ bonding
between the vacant d-orbitals on phosphorus and the
π-electrons of the benzene ring:
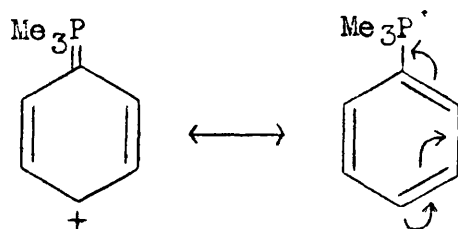
In the case of the nitration of trimethyl-
benzylammonium and trimethylbenzylphosphonium

picrates the inductive order is observed, since resonance effects cannot operate through the saturated carbon atom interposed between the ring and the phosphorus atom.

The iso-electronic $-SiMe_3$ group has also been shown to exhibit similar interaction between the ring and its $\underline{d}$-orbitals. Thus, the acid, Me_3SiCH_2COOH is markedly weaker than its carbon analogue Me_3CCH_2COOH indicating that the trimethylsilyl group has a strong +I effect.[97] However, $\underline{p}$-trimethylsilylbenzoic acid is only slightly weaker than benzoic acid, showing that any +I effect is opposed by some electron-withdrawing influence. The only interaction possible is a -T effect, operating through the vacant $\underline{d}$-orbitals on silicon and the π-electrons of the benzene ring.[98]

(b) Diethoxyphosphoro-group

The $\underline{p}$-OP(O)(OEt)$_2$ group has an overall electron-withdrawing influence that may be attributed to a -I effect but the lone-pair on the oxygen atom, between the phosphorus atom and the aromatic ring, can enter into resonance with the ring, hence activating the para-position by +T effect:
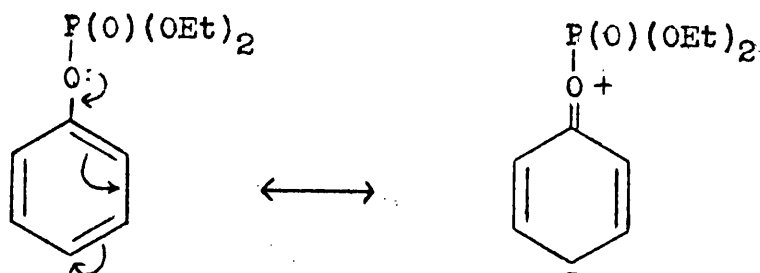
$\underset{\displaystyle}{P}(O)(OEt)_2$ ... $\underset{\displaystyle}{P}(O)(OEt)_2$

With the m-OP(O)(OEt)$_2$ group this activation cannot

occur, thus explaining why the reactivities of the

two positions differ by a factor of approximately 32.

This result is in accordance with nitration

data, when the group was found to be o/p directing.[57]

No attempt was made to examine the effect of this

substituent from the ortho-position, since the result

would be complicated by steric factors.

The behaviour of this substituent is

analogous to that of the chloro-group. By virtue

of its electronegativity this substituent is found

to deactivate, but its lone-pair electrons may

conjugate with the para-position. In protodesilyl-

ation the para-position is 16 times more reactive

than the meta-positions.[81]

(o) Substituents containing the phosphoryl bond

Substituents containing the phosphoryl

bond -P(O)R$_2$-(R = Ph, Me, OEt, OH) will be

considered as a group. Each of these was found to be strongly electron-withdrawing from both the para- and meta-positions. However, for an individual substituent, the para-position was found to be less reactive than the meta-position.

The observed order of reactivity was:

$$p\text{-}P(O)Ph_2 \; \langle \; p\text{-}P(O)Me_2 \; \langle \; p\text{-}P(O)(OEt)_2 \; \langle \; p\text{-}P(O)(OH)_2$$
$$\langle m\text{-}P(O)Ph_2 \; \langle \; m\text{-}P(O)(OEt)_2 \; \langle \; m\text{-}P(O)(OH)_2$$
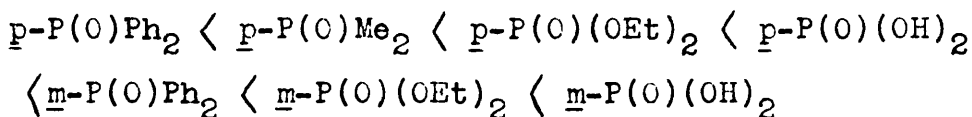
The strong deactivating influence and higher reactivity of the meta-position with these substituents is in agreement with reported nitration data.

The results, however, are complicated by an apparent dependence on the acid concentration of the medium. Thus, the relative rates obtained for $m\text{-}PO(OEt)_2$ and $m\text{-}PO(OH)_2$ were higher in $16.3\underline{M}$ sulphuric acid than in $18.4\underline{M}$ sulphuric acid (table VIII).

Table VIII. Variation of k_{rel} with sulphuric acid concentration

Substituent	$10^4 \; k_{rel}$	
	$(18.4\underline{M} \; H_2SO_4)$	$(16.3\underline{M} \; H_2SO_4)$
$m\text{-}PO(OEt)_2$	5.74	9.94
$m\text{-}PO(OH)_2$	9.63	13.2

A similar variation in $\underline{k}_{rel}$ for the meta-
and para-carbmethoxy and carboxy substituents, with
increase in acid concentration, has been reported by
Greasley.[80] The decrease in $\underline{k}_{rel}$ was thought to be
due to protonation of the weakly basic carbonyl group,
resulting in the strongly deactivating species:

$$-\overset{+}{\underset{}{C}}\underset{OR}{\overset{OH}{<}}$$
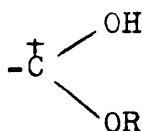
(R = Me or H).

It was proposed that the extent of the
protonation increased in going from the weaker to
the stronger acid medium, causing a decrease in $\underline{k}_{rel}$.
However, it was not established that protonation was
occurring, or, if it was, to what extent.

In the present kinetic studies on the
cleavage of aryltrimethylsilanes containing phosphoryl-
substituents, it was found that the observed optical
densities, at $t = \infty$, were far higher than the calculated
values obtained from the spectrum of the product in
glacial acetic acid. This prompted an investigation
of the ultraviolet spectrum of triphenylphosphine

oxide in glacial acetic acid solution, to which
various amounts of 18.4$\underline{M}$ sulphuric acid had been
added. The observed spectra are given in fig. VI,
p. 118. It has been pointed out that the phosphoryl
bond is highly polar[99] and it is reasonable to
assume that the increased absorption is due to the
presence of the species, Ph$_3$POH$^+$. Also, as the
intensification in the spectrum appears to be at a
maximum at 28.1% sulphuric acid, it is assumed that
triphenylphosphine oxide is fully protonated in this
medium.

Spectrum changes upon protonation are well-
known for aromatic systems containing polar groups,
and have been used in conjunction with acidity
function data to give a quantitative measurement
of the basicity of benzophenones[100], benzoic
acids[101], benzamides[102], etc. A more detailed
discussion of the protonation of polar groups will
be given later (p. 59).

As most of the phosphoryl-containing
substituents were cleaved in approximately 60 wt.%
sulphuric acid-glacial acetic acid solutions, it
is certain that they were present as the fully

protonated species, since the basicity of the
phosphoryl bond is not expected to vary a great
deal upon variation of the R groups in $-P(O)R_2$.

The only reported quantitative estimate
of the effect of a phosphoryl-containing substituent
is that made by Jaffe and Freedman[52], who have
determined σ-constants for the m- and p-$P(O)(OEt)_2$
groups (table III, p.19). Using their figures for
m-$P(O)(OEt)_2$, $\sigma = 0.55$ and the ρ-value of -4.69 for
protodesilylation in sulphuric acid-glacial acetic
acid, obtained when log k_{rel} is plotted against σ^+,
a k_{rel} of 2.63×10^{-3} is predicted.[81] (This
treatment is reasonable since it has been found
experimentally that $\sigma = \sigma^+$ for meta-substituents.[103])
The observed k_{rel} in 18.4$\underline{M}$ sulphuric acid-glacial
acetic acid was 5.74×10^{-4}, i.e. protonation
apparently brings about a five-fold reduction in
rate.

Owing to the similarity of the structures
of the substituents it does not seem unreasonable
to assume that for all of the substituents examined
the increase in deactivation is of the same order.

It is to be noted that resonance is still

important in these substituents since the meta-position is less deactivated than is the para-position. This is not surprising since upon protonation phosphoryl-containing substituents become hydroxyphosphonium cations and resonance can occur in these, as it does with the $-PMe_3^+$ substituent.

When the substituents $-P(O)(OEt)_2$ and $-P(O)(OH)_2$ were removed from the benzene ring, by one saturated carbon atom, the expected inductive order of withdrawal was observed, the meta-position being more deactivated than the para-position. It is not expected that protonation is affecting the result, since the sulphuric acid concentration is quite low.

Table IX. The alkaline cleavage of some phosphorus-substituted benzyltrimethyl-silanes ($RC_6H_4CH_2SiMe_3$).

Substituent (R)	[NaOH]	$k_1 \times 10^{-1} min.^{-1}$	k_g min.$^{-1}$mole^{-1}l.	k_{rel}
p-PMe_3^+	5.5×10^{-3}	60.5	12.5	3.56×10^5
p-$P(O)Ph_2$	0.1027	43.7	4.36×10^{-1}	1.26×10^4
p-$PO(OEt)_2$	0.1027	36.3	3.62×10^{-1}	1.04×10^4
p-$P(O)Me_2$	0.1027	11.2	1.12×10^{-1}	3.24×10^3
m-PMe_3^+	0.4090	51.8	1.30×10^{-1}	3.76×10^3
m-$P(O)Ph_2$	1.027	7.55	7.54×10^{-3}	2.17×10^2
m-$P(O)Me_2$	1.027	4.03	4.02×10^{-3}	1.16×10^2
m-CF_3 (1)	1.027	3.27	3.26×10^{-3}	9.45×10
m-Cl	1.027	1.93	1.92×10^{-3}	5.5×10

(1) k_{rel} for this substituent was supplied by Mr. B. M. Rushton.[91]

3. The Cleavage of some Phosphorus-substituted
Benzyltrimethylsilanes in Aqueous-methanolic Sodium
Hydroxide Solution

In order to obtain measurements of
substituent effects free from the effects of
protonation, the alkaline cleavage of the benzyl-
silicon bond in a number of phosphorus-substituted
benzyltrimethylsilanes was investigated.

The reaction was carried out under
conditions similar to those described by other
workers so that sensible comparisons could be made
between their results and the results obtained for
phosphorus-containing substituents. The results of
this study are summarised in table IX.

Relative rate constants were calculated
from data kindly supplied by Mr. B. M. Rushton,
vis. k_{rel} for the _m_-CF_3 compound, cleaved under
identical reaction conditions.

Substituent effects

Parker and Eaborn[88] showed that the
cleavage of benzyltrimethylsilanes exhibited a

Table X. Substituent constants for phosphorus-
containing groups

Phosphorus group	Substituent constant	
	para (σ^-)	meta (σ)
$-PMe_3^+$	+1.13	+0.73
$-P(O)Ph_2$	+0.84	+0.48
$-P(O)(OEt)_2$	+0.82	
$-P(O)Me_2$	+0.72	+0.42

marked dependence on substituent effects, electron-
withdrawing substituents causing a large increase
in reactivity. Further to this they demonstrated
that an excellent correlation existed between the
observed rate of cleavage and σ-constants, provided
that σ^--constants were used where applicable. Thus,
the reaction is extremely sensitive to tautomeric
electron-withdrawal.

The observed order of reactivity for the
substituents considered was:

$\underline{p}$-PMe$_3^+$ $\rangle$ $\underline{p}$-P(O)Ph$_2$ $\rangle$ $\underline{p}$-PO(OEt)$_2$ $\rangle$ $\underline{m}$-PMe$_3^+$ $\rangle$ $\underline{p}$-P(O)Me$_2$
$\rangle$ $\underline{m}$-POPh$_2$ $\rangle$ $\underline{m}$-P(O)Me$_2$ $\rangle$ $\underline{m}$-CF$_3$ $\rangle$ $\underline{m}$-Cl $\rangle\!\rangle$ $\underline{m}$-PO$_3^=$ and $\underline{p}$-PO$_3^=$
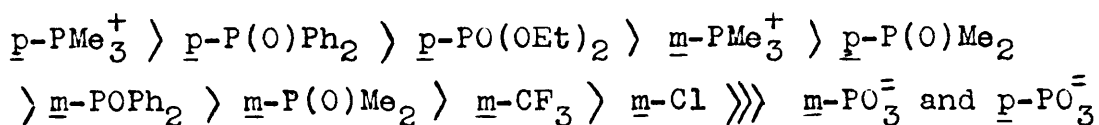
Using $\rho = 4.89$, the reaction constant determined by
Parker and Eaborn[88], substituent constants (σ) for
these groups have been calculated (table X). In the
case of $\underline{para}$-substituents the substituent constant
is σ^-, and for $\underline{meta}$- it is σ.

It was not possible to examine the effect
of the $\underline{m}$-PO(OEt)$_2$ substituent, since the alkali
concentration required for the cleavage reactions
would also cause hydrolysis of the ester groupings.
This was demonstrated by the observation that the

spectrum of diethyl phenylphosphonate in 39 wt.%
aqueous methanol, to which 1.027$\underline{N}$ sodium hydroxide
had been added, changed considerably over ten hours
(the time estimated for completion of the cleavage
reaction). It is reasonable to assume that diethyl
$\underline{m}$-trimethylsilylmethylphenylphosphonate would
hydrolyse at a similar rate. When a sample of
diethyl phenylphosphonate, in 39 wt.% aqueous
methanol, was treated with 0.1027$\underline{N}$ sodium hydroxide
an extremely small drop in optical density occurred
over ten hours, indicating that hydrolysis would
not affect the rate measured for the cleavage of
the para-compound.

(a) Trimethylphosphonium group

The order of reactivity observed for the
$-PMe_3^+$ substituent was $\underline{p} \rangle \underline{m}$, the relative rate
constants being 3.56 x 10^5 and 3.76 x 10^3. Thus,
when the substituent is in the para-position it is
strongly activating, being only five times less
effective than the $\underline{p}$-NO_2 group. The large difference
in reactivity between the meta- and para-positions
is a clear indication of the importance of resonance
effects. Thus through its vacant $\underline{d}$-orbitals the

$\underline{p}$-PMe$_3^+$ group can stabilise the separating anion in the following way:

$$\bar{C}H_2-C_6H_4-PMe_3^+ \longleftrightarrow CH_2=C_6H_4=PMe_3$$
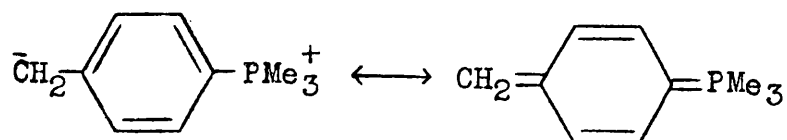
Such resonance cannot operate from the <u>meta</u>-position, which accounts for the large difference in reactivity.

Although it is the first time that this phenomenon has been demonstrated for phosphonium ions in aromatic systems, similar resonance was observed with the -SMe$_2^+$ substituent.[104] It was found that this substituent belongs to the class which requires $\bar{\sigma}$-constants to describe its effect on the ionisation of phenolic -OH. The $\underline{p}$-dimethyl sulphonium ion conjugates with the reaction site in the following manner:

$$HO-C_6H_4-SMe_2^+$$

Phosphorus $\underline{d}$-orbital resonance has, however, been shown to occur in non-aromatic systems.

Doering and Hoffman[105] found that in the deuteroxide

catalysed exchange reaction of tetramethyl "onium"

iodides, tetramethylphosphonium iodide exchanged

73.9% of its hydrogen atoms after 3 hr. at $62°$.

Under similar conditions, tetramethylammonium iodide

gave no observable change after 504 hr. The following

mechanism for the reaction was postulated:

$$\overset{+}{Me_3P}\text{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\text{-}H \xrightarrow{\ OD^-\ } \left[Me_3\overset{+}{P}\text{-}CH_2^- \longleftrightarrow Me_3P = CH_2 \right]$$

$$\Big\downarrow D_2O$$

$$Me_3\overset{+}{P}CH_2D$$
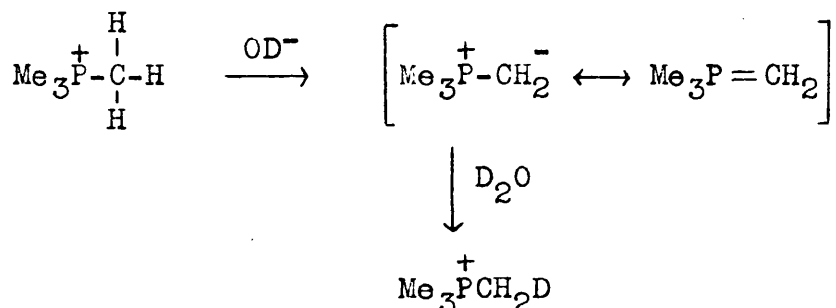
In the case of tetramethylammonium iodide, resonance

stabilisation of the transition state cannot occur

since nitrogen cannot expand its octet.

(b) <u>Substituents containing the phosphoryl bond</u>

Substituents containing the phosphoryl

bond were found to be strongly activating from both

the <u>meta</u> and <u>para</u>-positions.

Jaffe and Freedman[52] have determined

the σ^--constant for $p\text{-}PO(OEt)_2$ (table III, p.19)

Their value of +0.84 predicts a relative rate
constant of 1.28×10^4, which agrees reasonably
well with the observed $\underline{k}_{rel}$ of 1.04×10^4.

The strong activating influence of these
substituents is intimately related to the character
of the phosphoryl bond. It has been proposed that
the phosphorus-oxygen bond is semi-polar, modified
by back coordination from oxygen to phosphorus,
giving it some multiple bond character, [62] and as
a consequence may be considered as a resonance
hybrid of structures which include the following:

$$R_3P = O \longleftrightarrow R_3\overset{+}{P} - \overset{-}{O}$$
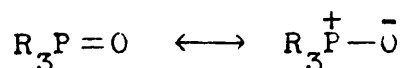
Thus, much of the electron-withdrawing
influence of substituents containing the phosphoryl
group is derived from this formal positive charge
on phosphorus, giving rise to a strong -I effect.
However, even if the positive charge were a full
one, the substituents would not have the strong
activating influence of the $-P\overset{+}{M}e_3$ substituent due
to the negative end of the phosphoryl dipole.

Variation in reactivity within the series
$-P(O)R_2$ may be conveniently explained in terms of

electron supply and withdrawal by the substituent R.
The observed order of activation from the para-
position was:

$$-P(O)Ph_2 \rangle \ -PO(OEt)_2 \rangle \ -P(O)Me_2$$
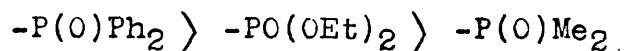
The phenyl group and the ethoxy group
may increase electron density on phosphorus by +T
effect. The former, by overlap between phosphorus
d-orbitals and the π-cloud of the aromatic nucleus,
and the latter, by overlap between non-bonding
electrons on oxygen and phosphorus d-orbitals.
However, in both these cases the +T effect is opposed
by a -I withdrawal of electrons. Electron supply in
R would cause a decrease in the formal positive
charge on oxygen, and consequently a decrease in
activation. In the case when R = Me, this group
can only supply electrons inductively by a moderate
+I effect.

(c) The phosphono anions

No cleavage of benzyltrimethylsilanes
containing the $-PO_3^=$ substituent in either the meta-
or the para-position could be detected spectrophoto-
metrically. The σ-constant for the $p-PO_3^=$ substituent

(-0.16) [50] predicts a half-life for the cleavage reaction at 50° in 1.0$\underline{N}$ sodium hydroxide solution of ca. 2.6 x 10^3 hr. Thus, it is not surprising that no cleavage was detected in 96 hr. The σ-constant for m-$PO_3^{=}$ (-0.02) [50] indicates a reactivity slightly lower than that of the unsubstituted benzyltrimethylsilane. The fact that no cleavage was observed in four days indicates that the substituent is more deactivating than the σ-constant would suggest.

The strong deactivating influence of this substituent is due to its double negative charge, resulting in an extremely high +I effect.

The effect of variation in alkali concentration on the cleavage of compounds containing charged substituents

Eaborn and Parker[88] found that the specific rate constant for uncharged species was independent of the alkali concentration, while for benzyltrimethyl-silanes containing the carboxylate anion, there was a rise in specific rate constant with increase in alkali concentration. They demonstrated that this

rise was due to an increase in ionic strength of the medium, and that at low ionic strengths, the Brønsted-Bjerrum relationship[106] was obeyed.[93]

Brønsted and Bjerrum showed that the rate of a reaction between two ions is related to the ionic strength of the medium, according to the following relationship:

$$\log_{10} k = \log_{10} k_o + 2AZ_a Z_b \mu^{\frac{1}{2}}$$

where k_o is the rate constant at infinite dilution, A is the constant of the Debye-Huckel equation, Z_a and Z_b are the charges on the reacting ions and μ is the total ionic strength.

The relationship predicts an increase in specific rate constants with increase in ionic strength, for a reaction between ions of the same sign. This, in fact, was observed by Eaborn and Parker in the reaction of OH^- with the trimethyl-benzoic anions.[93]

For species of opposite sign, increasing ionic strength would result in a decrease in specific rate constant. This was observed in the cleavage of

of the positively charged trimethyl-$\underline{m}$-trimethyl-
silylmethylphenylphosphonium iodide by OY^- ($Y = H$
and Me) (table XI).

Table XI. The variation of specific rate constant
for the cleavage of $[Me_3SiCH_2C_6H_4PMe_3^+]I^-$
in solutions of varying alkali concentration

$[NaOH]$ $\underline{N}$	$10^3\underline{k}_1$ $(min.^{-1})$	$10^{-3}\underline{k}_s$ $(min.^{-1}mole^{-1}l.)$
0.204	26.8	1.345
0.409	51.8	1.30
0.535	66.5	1.28
0.775	95.5	1.26
1.027	128.9	123.5

A physical interpretation of the Brønsted-
Bjerrum relationship may be made as follows.
According to the qualitative theory of solvent
effects, of Hughes and Ingold,[92] "an increase in
the solvating power of the medium will accelerate
the creation and concentration of charges and
inhibit their destruction and diffusion." In a
reaction between ions of the same sign there is
a concentration of charge in the transition state

and as a consequence the reaction will go faster

in a better ion-solvating medium. Conversely, in

a reaction between ions of opposite charge there

is a destruction of charge in the transition state

and the reaction will go more slowly when the

polarity of the medium is higher.

An increase in ionic strength is equivalent

to an increase in solvent polarity, since ions may,

in effect, be solvated by being surrounded by ions

of the opposite charge.

4. The Protonation of Triphenylphosphine Oxide in
Strongly Acidic Media

As was pointed out above, the ultraviolet
spectrum of triphenylphosphine oxide changed
considerably with variation in sulphuric acid
concentration in acetic acid-sulphuric acid mixtures
(fig. VI p.118). Such changes were interpreted as
being due to protonation of the phosphoryl bond in
triphenylphosphine oxide. Examination of the
curves obtained when λ_{268} and λ_{274} was plotted
against wt.% sulphuric acid indicates that
protonation is complete when 28.1 wt.% sulphuric
acid is reached.

In order to obtain quantitative information
on the basicity of the phosphoryl bond in triphenyl-
phosphine oxide, it was necessary to examine the
spectral changes in a medium, the acidity function
(H_O) of which was known.

The acidity function (H_O) was proposed
by Hammett and Deyrup[77] to describe the behaviour
of weak, neutral bases in aqueous sulphuric acid
solutions.

Thus for the equilibrium:
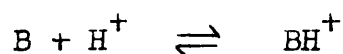
$$B + H^+ \rightleftharpoons BH^+$$

H_0 is defined by the following relationship:

$$H_0 = pK_{BH^+} - \log \frac{[BH^+]}{[B]} \qquad \ldots\ldots\ldots\ldots(1)$$

(It may be shown that $H_0 = -\log \dfrac{a_{H^+} f_B}{f_{BH^+}}$)

Where the ultraviolet spectrum of the base (B) measured in one acid concentration differs from the spectrum of the conjugate acid, measured at a higher concentration, determination of the spectrum in all intermediate acid concentrations gives a direct measure of the percentage protonation at these concentrations. The ratio $[BH^+]/[B]$ may also be obtained from these observations, since it can be shown that $[BH^+] = \epsilon - \epsilon_B$ and $[B] = \epsilon_{BH^+} - \epsilon$, for a particular wavelength.

In the present studies the spectrum of triphenylphosphine oxide was measured in aqueous sulphuric acid solutions covering the range -1.0 - -7.1 H_0 units (fig.IV p.117) when ϵ_{268} and ϵ_{274} was plotted versus H_0, typical sigmoid

Table XII. The pK_a values of neutral substrates

measured in sulphuric acid

Substrate	pK_a
Benzamide [102]	-2.16
Acetophenone [107]	-6.15
Benzophenone [100]	-6.18
Benzoic acid [101]	-7.26
p-Nitrotoluene [108]	-10.96
Nitrobenzene [109]	-11.26
m-Chlorobenzene [108]	-12.27

neutralisation curves were obtained (fig. V ,p.117)

The pK_{BH^+} (i.e. the pK_a of the conjugate acid

$Ph_3\overset{+}{P}OH$) is equal to the value of H_o at the point

of inflexion on these curves, since from the

relationship (1) the term $\log \frac{[BH^+]}{[B]}$ becomes zero

at this point and $H_o = pK_{BH^+}$. The mean of the

values of pK_{BH^+} determined at 268 mµ and 274 mµ was

-3.65 units.

This technique has been used by several

authors to determine pK_a values for a wide range of

aromatic compounds. The pK_a values of some neutral

substrates, measured spectrophotometrically, are

given in table XII.

From equation (1) defining H_o it can be

seen that a plot of $\log \frac{[B]}{[BH^+]}$ versus H_o should be a

straight line of unit slope. When $\log \frac{[B]}{[BH^+]}$,

obtained from the extinction coefficients at 268 mµ

and 274 mµ, was plotted against H_o (see fig. VIII and

table XIII) straight lines were obtained, the slopes

of which were 0.685 (at 268 mµ) and 0.666 (at 274 mµ).

Previous workers have also observed

similar departures from the theoretical slope in

Table XIII. Values of $\log\frac{[B]}{[BH^+]}$ and H_0 for triphenyl-
phosphine oxide in sulphuric acid

	$\log\frac{[B]}{[BH^+]}$	
H_0	268 mμ	274 mμ
-5.5	$\bar{2}$.4713	$\bar{2}$.7709
-4.75	$\bar{1}$.1038	$\bar{1}$.3032
-4.17	$\bar{1}$.5551	$\bar{1}$.7042
-3.67	$\bar{1}$.9455	0.7755
-3.50	0.0719	0.1987
-3.27	0.1959	0.3324
-2.95	0.3820	0.5092
-2.60	0.5922	0.7419
-1.70	1.1523	1.3118

Fig. VIII Plots of log $\frac{[B]}{[BH^+]}$ against H_0 for determinations at (a) 268mμ and (b) 274mμ
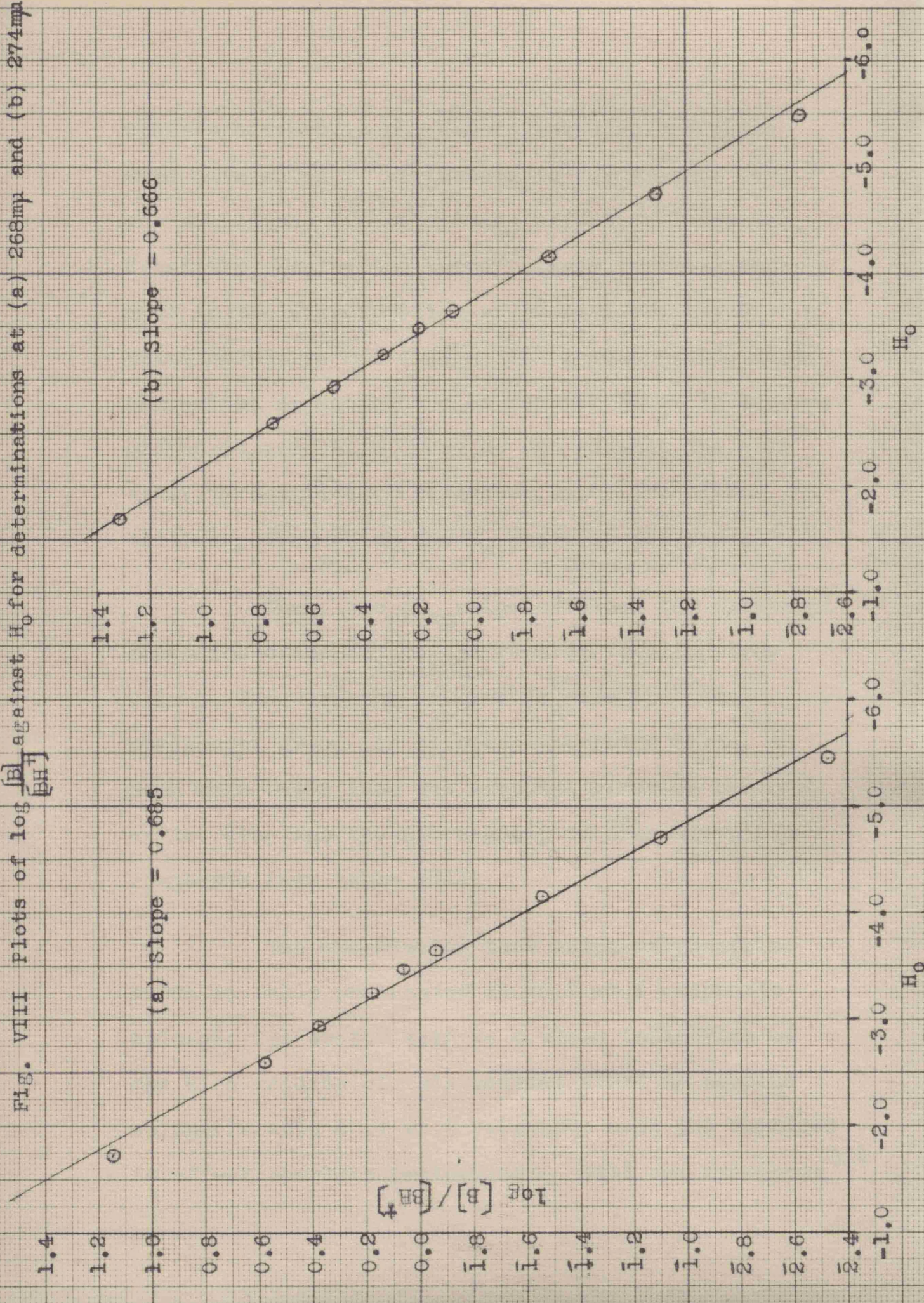
spectrophotometric pK_a determinations, and these were attributed to variations in the spectra of the substrates due to solvent effect.[110] However, Katritzky, Waring and Yates[110] have recently shown that in the O-protonation of benzamides, the H_o relationship is not obeyed, and they conclude that benzamides do not behave as Hammett bases in aqueous sulphuric acid (i.e. they do not exhibit the same activity coefficient behaviour as do the nitro-anilines, from which the H_o scale is derived).

Thus, the pK_a value obtained for triphenyl-phosphine oxide may be far removed from the true value. However, the results do show that the phosphoryl group, in triphenylphosphine oxide, is much more basic than the carbonyl group in benzoic acids, etc. and the nitro-group in aromatic nitro-compounds (see table XII).

The observation that triphenylphosphine oxide is fully protonated in 28.1 wt.% sulphuric acid-glacial acetic acid is a clear indication of the high acidity of this medium, since in aqueous sulphuric acid 80.1 wt.% sulphuric acid was required to effect complete protonation. Hall and Spengeman[111]

have determined the acidity function (H_o) for mixtures of 100% sulphuric acid in anhydrous acetic acid up to $8\underline{M}$ sulphuric acid. The H_o values obtained were far higher than those for aqueous sulphuric acid solutions of equivalent concentration (e.g. H_o = -3.01 for $1\underline{M}$ sulphuric acid in glacial acetic acid compared with H_o = -0.26 for $1\underline{M}$ aqueous sulphuric acid).

Since triphenylphosphine oxide was fully protonated in 28.1 wt.% sulphuric acid-glacial acetic acid, it is obvious that this medium (which contains 2-3% water) has an acidity comparable with that of the anhydrous mixture used by Hall and Spengeman.[111]

EXPERIMENTAL SECTION

EXPERIMENTAL

1. General Techniques.

The preparation of Grignard reagents was
carried out in a three-necked flask fitted with a
rubber sealed stirrer (lubricated with silicone oil
or grease), a double surface condenser and a dropping.
funnel. Sulphuric acid bubblers were used to exclude
moisture and, in the case of Grignard reagents
prepared in tetrahydrofuran, a nitrogen inlet tube
was fitted. Anhydrous ether, supplied by MacFarlan
and Co. Ltd., was dried over sodium wire before use.
Tetrahydrofuran (THF) was dried and freed from
peroxides by refluxing with lithium aluminium hydride,
followed by distillation through a 12 inch Dufton
column. To prevent further peroxidation, THF,
purified in this way, was stored under nitrogen.
Hopkin and Williams's "Magnesium turnings for Grignard
reagents" were used after drying in an oven at 150°.
Initiation of the reaction was effected by addition
of a few drops of ethylene dibromide, followed by
cautious warming. After the coupling reaction was
completed the mixture was poured into a beaker
containing ice and 2N sulphuric acid, to hydrolyse

unreacted Grignard reagent. The organic layer was separated and usually dried over anhydrous sodium sulphate.

Organo-lithium reagents were prepared in a similar apparatus to that described for Grignard reagents. Lithium metal was hammered into a foil 1 mm. thick and then cut into pieces approximately 5x5 mm. in size. The reaction was always carried out under a slow stream of oxygen-free nitrogen, dried by passing through concentrated sulphuric acid. After formation of the organo-lithium reagent its ethereal solution was filtered into a dropping funnel through a glass wool plug. Hydrolysis was again effected by pouring the reaction mixture onto ice and $2\underline{N}$ sulphuric acid.

Wurtz-Fittig reactions were carried out by addition of a mixture of trimethylchlorosilane and the appropriate aryl-halide to molten sodium metal in boiling sulphur-free toluene. The rate of addition was such as to maintain constant refluxing. After all of the mixture of halides had been added the mixture was refluxed for 1 hr. Precipitated sodium chloride was filtered off and the filtrate washed with water,

dried over anhydrous sodium sulphate and finally fractionated.

Fractionations were carried out on a precision-made 100 cm. Vigreux column, unless otherwise stated. For removal of solvents a 70 cm. glass-helices-packed column was used. Both columns were enclosed in an electrically heated jacket.

Distillation at reduced pressure was carried out using a Pulsometer vacuum pump, capable of giving a pressure of 0.2 mm. For distillation requiring lower pressures (0.2 - 0.01 mm.) an Edwards, two-stage, air-ballast vacuum pump was used. Bumping at reduced pressure was minimised by the use of a magnetic stirrer and "flea", or with wooden anti-bumping sticks.

Micro-analyses, for carbon and hydrogen, were determined by Drs. Wieler and Strauss, of Oxford, or by Dr. Bernhardt, of Mulheim, Ruhr, West Germany. Hydrolysable chlorine was determined by Volhard's method.

Melting points and boiling points are quoted uncorrected.

2. The Preparation of Arylsilicon Compounds containing Phosphorus.

(a) Preparation of organosilicon compounds.

p-Bromophenyltrimethylsilane.- The Grignard reagent
from p-dibromobenzene (284 g., 1.0 mole) and
magnesium (24.3 g., 1.0 g.-atom) was prepared in
ether (500 ml.). Trimethylchlorosilane (109 g.,
1.0 mole) in ether (150 ml.), was added over 0.5 hr.
Fractionation, after working up in the usual way,
gave 130 g. of a liquid, b.p. 120-127°/20 mm., which
deposited crystals on standing. These crystals
(mostly p-bis-phenyltrimethylsilane) were filtered
off and refractionation of the mother liquor gave 90 g.
(45%) of p-bromophenyltrimethylsilane, b.p. 228-229.5°,
n_D^{25} 1.5250 (lit.,[112] 229.5°/752 mm., n_D^{22} 1.5229).

p-Chlorophenyltrimethylsilane.- The Grignard reagent
from p-chlorobromobenzene (210.6 g., 1.1 mole) and
magnesium (26.7 g., 1.1 g-atom) was prepared in ether
(500 ml.). Trimethylchlorosilane (109 g., 1.0 mole),
in ether, was added over 0.5 hr. and the mixture
refluxed for 20 hr. Working up in the usual way gave
114.5 g. (62%) of p-chlorophenyltrimethylsilane, b.p.

88-92°/15-17 mm., n_D^{25} 1.5081 (lit.,[113] 98-100°/15-17
mm.).

Similarly prepared was:

m-Chlorophenyltrimethylsilane.- 73% yield, b.p. 86-
88°/12 mm., n_D^{25} 1.5090 (lit.,[114] 100.5°/22 mm., n_D^{25}
1.5099).

p-Tolyltrimethylsilane.- A mixture of p-chlorotoluene
(63.3 g., 0.5 mole) and trimethylchlorosilane (54.3 g.,
0.5 mole) was added to sodium (25.3 g., 1.1 g-atom)
in refluxing toluene and the mixture was refluxed for
1 hr. The sodium chloride was filtered off and
fractionation of the mother liquor gave 61 g. (60%)
of p-tolyltrimethylsilane, b.p. 189-190°, n_D^{25} 1.4896
(lit.,[115] b.p. 192°, n_D^{20} 1.4910).

Similarly prepared was:

m-Tolyltrimethylsilane.- 67% yield, b.p. 186-188°
n_D^{25} 1.4902 (lit.,[116] b.p. 190°, n_D^{25} 1.4902).

p-Trimethylsilylbenzylbromide.- This compound was
prepared by the method of Soverson, Roscup, Lindberg
and Engberg.[117]

p-Tolyltrimethylsilane (44.g., 0.27 mole), N-bromo-

succinimide (44.5 g., 0.25 mole) and benzoyl peroxide

(0.3 g.) in carbon tetrachloride (130 ml.) were

heated to gentle reflux. After initiation the

reaction became vigorous and the heating was removed

until refluxing subsided. Heating was then resumed

and the mixture was refluxed for a further 2 hr.

The solution was then filtered, washed with 5%

sodium hydroxide solution and finally with water.

Fractionation on a 12 inch Vigreux column gave 37 g.

(55%) of p-trimethylsilylbenzylbromide, b.p. 114-

118°/8-9 mm., n_D^{25} 1.5412 (lit., b.p. 128-129°/12 mm.,

n_D^{20} 1.5400).[117]

Similarly prepared was:

m-Trimethylsilylbenzylbromide.- 60% yield, b.p. 126-

127°/12 mm., n_D^{25} 1.5415 (lit.,[117] 128-129°/13 mm.,

n_D^{20} 1.5379).

p-Trimethylsilylphenol.- This was prepared by the

method of Speier.[118]

(a) p-Chlorophenol (128.6 g., 1.0 mole) and

trimethylchlorosilane (163 g., 1.5 mole) were

refluxed together for 6 hr. Fractionation of the

mixture gave 180 g. (90%) of p-chlorophenoxytrimethyl-

silane, b.p. 101°/13 mm., n_D^{25} 1.4955 (lit.,[118] 101°/
14 mm., n_D^{25} 1.4923).

(b) A mixture of trimethylchlorosilane (59.25 g.,
0.5 mole) and p-chlorophenoxytrimethylsilane (100.25 g.,
0.5 mole was added to sodium (25 g., 1.08 g-atom)
in refluxing toluene. After filtration (to remove
the sodium chloride), fractionation gave 89 g. (80%)
of p-trimethylsilylphenoxytrimethylsilane, b.p. 140-
142°/38 mm., (lit.,[118] 132°/25 mm.)

(c) p-Trimethylsilylphenoxytrimethylsilane (50.0 g.)
was hydrolysed by heating, for 0.5 hr. on a water
bath, in 95% aqueous ethanol (28 g.) to which 2 drops
of concentrated hydrochloric acid had been added.
This solution on dilution and extraction with ether
gave 32 g. of crude p-trimethylsilylphenol, which
was used in the preparation of diethyl-p-trimethyl-
silylphenylphosphate without further purification.

Similarly prepared was:
m-Trimethylsilylphenol.- m-Trimethylsilylphenoxy-
trimethylsilane, supplied by Dr. K. Leyshon, was
hydrolysed to m-trimethylsilylphenol as described
above. The crude product was used in the
preparation of diethyl-m-trimethylsilylphenylphosphate.

(b) The preparation of organophosphorus compounds.

Diethylphosphorochloridate.- Phosphorus trichloride
(0.5 mole) in benzene (150 ml.) was added to
absolute ethanol (1.5 mole) in benzene (200 ml.),
the temperature of the reaction mixture being kept
below 10°. Sulphuryl chloride (0.5 mole) was then
added dropwise over 1 hr. Removal of the volatiles
on a steam bath, at water-pump pressure, left a
liquid which was distilled to give 55.5 g. (65%)
of diethylphosphorochloridate, b.p. $80-81^{\circ}/8$ mm.,
n_D^{25} 1.4140 (lit.,[119] $86^{\circ}/12$ mm., n_D^{25} 1.4162).

Diethyl phenylphosphonate.- Phenyl-lithium,
prepared from bromobenzene, (18.8 g.) and lithium,
(1.68 g.) was added to diethyl phosphorochloridate
(17.2 g.) in ether (50 ml.), the reaction temperature
being kept below 5°. The mixture was allowed to
stand overnight, and, on working up in the usual way,
gave 9 g. (45%) of diethylphenylphosphonate, b.p.
$132-134^{\circ}/4.5$ mm., n_D^{25} 1.4932 (lit.,[6] $117.8^{\circ}/1.5$ mm.,
n_D^{25} 1.4935).

Diethyl benzylphosphonate.- Diethyl phosphonate

(27.6 g., 0.2 mole) in light petroleum (30 ml.) was
added to sodium (4.6 g., 0.2 g.-atom) in light
petroleum (100 ml.). The mixture was refluxed until
all the sodium had reacted. Benzyl chloride (25.2 g.,
0.2 mole) in light petroleum (30 ml.) was added and
the mixture refluxed for 4 hr. Fractionation gave
20 g. (50%) of diethyl benzylphosphonate, b.p. 157°/
14 mm., n_D^{25} 1.4945 (lit.,[120] 155°/14 mm.).

Diethylphenylphosphate.- Phenol (13 g. 0.18 mole)
in ether (50 ml.) was added to sodium (4.14 g.,
0.18 g.-atom) in ether. The mixture was refluxed
until the solution of the sodium was complete (1 hr.).
Diethylphosphorochloridate (30.6 g., 0.18 mole) in
ether was added, and the mixture refluxed for 15 hr.
The ether was removed and the oil obtained was
fractionated to give 12 g. of diethylphenylphosphate,
b.p. 144-145°/5 mm., n_D^{25} 1.4755 (lit.,[121] 200-230°/
70 mm.).

(c) The preparation of arylsilicon compounds
containing phosphorus.

Attempted free-radical phosphonation of
phenyltrimethylsilane.- Phenyltrimethylsilane (45.5 g.,
0.325 mole) and dimethylphosphonate (35.8 g., 0.325
mole) were mixed and heated to $140-150^{\circ}$. Di-t-butyl
peroxide (47.5 g., 0.325 mole) was added at a rate of
approximately 1 g./10 min. During the later stages
of the reaction the liquid temperature fell to
approximately 120°. The mixture was refluxed
overnight (to destroy unchanged peroxide) and the
two layers obtained were separated and each was
distilled. From the upper layer a fraction, 3 g.,
b.p. $96-98^{\circ}/0.5$ mm., n_D^{25} 1.4954, and from the lower
layer, 3 g., b.p. $96-98^{\circ}/0.5$ mm., n_D^{25} 1.4970, was
collected. The infra-red spectra of these were
identical and similar to the spectrum of diethyl
p-trimethylsilylphenylphosphonate. The two fractions
were combined and refractionated to give 4.5 g.,
b.p. $98-100^{\circ}/0.6$ mm., n_D^{25} 1.4956. Hydrolysis of 2 g.
of this product, by refluxing with concentrated
hydrochloric acid for 5 hr., gave a white, crystalline
solid, which, on recrystallisation, from water, gave

plates, m.p. 162.5-163° (phenylphosphonic acid, m.p. 161-162°.).[3]

Diethyl p-trimethylsilylphenylphosphonate.- The Grignard reagent from p-chlorophenyltrimethylsilane (87 g., 0.5 mole) and magnesium (12.15 g., 0.5 g.-atom) was prepared in refluxing THF, the mixture being refluxed for 5 hr. after the addition of the halide. The solution of the Grignard reagent was added slowly to diethylphosphorochloridate (77.4 g., 0.45 mole) in anhydrous ether (150 ml.), the reaction mixture was then refluxed for 1 hr., allowed to cool and then hydrolysed with ice, dilute sulphuric acid and the organic layer removed. The aqueous layer was extracted with ether and the combined organic layers washed with 2N sodium hydroxide solution and finally with water. Rapid distillation of the oil, obtained after removal of the THF and ether, gave 106 g. of a colourless liquid, b.p. 120-125°/1.0 mm., fractionation of which gave 78 g. (60%) of diethyl p-trimethylsilylphenylphosphonate, b.p. 154-156°/2.5 mm., n_D^{25} 1.4933 (Found: C, 54.73; H, 8.31. $C_{13}H_{23}O_3PSi$ requires C, 54.55; H, 8.05%).

Similarly prepared was:

Diethyl m-trimethylsilylphenylphosphonate.- 60%, b.p. 142-143°/2.2 mm., n_D^{25} 1.4915 (Found: C, 54.06; H, 7.70%).

p-Trimethylsilylphenylphosphonic acid chloride.-
Diethyl p-trimethylsilylphenylphosphonate (14.2 g.,
0.05 mole) was refluxed with phosphorus pentachloride
(20.8 g., 0.1 mole) for 2 hr. Phosphoryl chloride
was distilled off and the residue was distilled to
give 9.5 g. (70%) of a pale, straw-coloured liquid,
b.p. 128-124°/1.12 mm., which crystallised on shaking
to give a white solid, m.p. 44-45° (Found: C, 38.75;
H, 4.68; Cl, 26.65. $C_9H_{13}Cl_2OPSi$ requires C, 40.4;
H, 4.87; Cl, 27.1%).

Similarly prepared was:

m-Trimethylsilylphenylphosphonic acid chloride.- 60%,
b.p. 131-132°/2.5 mm., n_D^{25} 1.5352 (Found: Cl, 26.5%).

p-Trimethylsilylphenylphosphonic acid.- p-Trimethyl-
silylphenylphosphonic acid chloride (4 g.) was
dissolved in acetone (10 ml.) and the solution was treat
treated with 2N sodium hydroxide until a clear
solution was obtained. The mixture was acidified
until precipitation of the acid was complete and then

extracted with ether. Evaporation of the ether gave a

crystalline residue which, after three recrystallis-

ations from 60-80° light petroleum, gave 2.5 g. (75%)

of white needles, m.p. 174-175° (Found: C, 46.49;

H, 6.33. $C_9H_{15}O_2PSi$ requires C, 46.95; H, 6.52%).

Similarly prepared was:

m-Trimethylsilylphenylphosphonic acid.- m.p. 96-98°

(Found: C, 46.67; H, 6.41%).

Attempted preparation of diphenyl-p-trimethylsilyl-

phenylphosphine oxide.

(a) Phenyl-lithium from bromobenzene (23.5 g., 0.15

mole) and lithium (2.1 g., 0.3 g.-atoms) at 0° and added

to diethyl p-trimethylsilylphenylphosphonate (14.2 g.,

0.05 mole). Working up in the usual way, after

refluxing for 5 hr., gave a non-crystalline solid

of unknown identity.

(b) A similar resinous solid was obtained by the

reaction of phenyl-lithium with p-trimethylsilyl-

phenylphosphonic acid chloride.

Diphenyl-p-trimethylsilylphenylphosphine oxide.- The

Grignard reagent from bromobemzene (9.42 g., 0.06 mole)

and magnesium (1.44 g., 0.06 g.-atom) was prepared

in anhydrous ether. To this was added p-trimethyl-
silylphenylphosphonic acid chloride (5.5 g., 0.022 mole)
in ether (20 ml.) and the mixture was refluxed for 2
hr. Working up in the usual way gave an oil which
crystallised slowly on a watch glass. Recrystall-
isation from 60-80° light petroleum gave white
crystals, m.p. 75-80°. Further recrystallisation
did not increase the melting point and so the compound
was chromatographed through a 12 inch alumina column
using benzene and 6:1 benzene/methanol as eluants.
The phosphine oxide was recovered from the solution and
one recrystallisation from 60-80° light petroleum
gave 5 g. of white crystals, m.p. 92-93° (Found:
C, 71.97; H, 6.69. $C_{21}H_{23}OPSi$ requires C, 72.0;
H, 6.56%).

Diphenyl-m-trimethylsilylphenylphosphine oxide.- The
same method was used as for the para-isomer. However,
on removal of the solvent, an oil was obtained which
would not crystallise. Distillation gave a viscous
oil, b.p. 212-215°/0.1 mm., which set to a glass on
cooling. On standing for three months the glass
crystallised (Found: C, 72.00; H, 6.53%).

Diethyl p-trimethylsilylbenzylphosphonate.- Diethyl

phosphonate (27.2 g., 0.2 mole) was added to sodium

(4.6 g., 0.2 g.-atom) in 60-80° light petroleum (50 ml.).

After complete solution of the sodium, p-trimethylsilyl-

benzylbromide (37.0 g., 0.18 mole) was added and the

mixture refluxed for 6 hr. Fractional distillation

(after the precipitated sodium bromide had been

removed) gave 30 g. (55%) of a liquid, b.p. 151-153°/

1.0 mm., n_D^{25} 1.4897 (Found: C, 55.95; H, 8.60.

$C_{14}H_{25}O_3PSi$ requires C, 55.9; H, 8.33%).

Similarly prepared was:

Diethyl m-trimethylsilylbenzylphosphonate.- 60%,

149-151°/2.3 mm., n_D^{25} 1.4885 (Found: C, 55.24;

H, 8.05%).

p-Trimethylsilylbenzylphosphonic acid.- Diethyl

p-trimethylsilylbenzylphosphonate (10.0 g., 0.033 mole)

was refluxed with phosphorus pentachloride (13.5 g.,

0.066 mole) for 4 hr. The phosphoryl chloride was

removed at the pump and distillation of the residue

gave 4 g. of liquid, b.p. 150°/2 mm., assumed to be

p-trimethylsilylbenzylphosphonic acid chloride.

This was dissolved in acetone (10 ml.) and treated

with 2N sodium hydroxide solution. The clear

solution was acidified, extracted with ether, and

the ether removed. The solid was recrystallised to white plates, m.p. 167-168° (Found: C, 48.88; H, 7.05. $C_{10}H_{17}O_2PSi$ requires C, 49.15; H, 6.96%).

Similarly prepared was:

m-Trimethylsilylbenzylphosphonic acid.- m.p. 144° (Found: C, 49.03; H, 6.88%).

Diethyl-p-trimethylsilylphenylphosphate.- To sodium ethoxide (0.18 mole) from sodium (4.14 g., 0.18 g.-atom) and ethanol (60 ml.) was added p-trimethylsilylphenol (30 g., 0.18 mole) in ethanol (60 ml.), followed by diethylphosphorochloridate (30.6 g., 0.8 mole) in benzene (60 ml.). The mixture was refluxed for 3 hr. and then poured into water and extracted with ether. Removal of the ether gave 20 g. (45%) of a liquid, b.p. 145-150°/2-2.5 mm., n_D^{25} 1.4840 (Found: C, 52.6; H, 7.69. $C_{13}H_{23}O_4PSi$ requires C, 51.8; H, 7.64%).

Similarly prepared was:

Diethyl-m-trimethylsilylphenylphosphate.- 50%, b.p. 148-150°/1.0 mm., n_D^{25} 1.4900 (Found: C, 51.28; H, 7.34%).

Dimethyl-p-trimethylsilylphenylphosphine oxide.- To the Grignard reagent from methyl iodide (42.6 g.,

0.3 mole) and magnesium (7.28 g., 0.3 g.-atom) in
anhydrous ether was added p-trimethylsilylphenyl-
phosphonic acid chloride (34.g., 0.125 mole) and the
mixture was refluxed for 2 hr. After hydrolysis, two
organic layers were obtained and the lower one of these
was removed and dissolved in chloroform. This solution
was dried over anhydrous sodium sulphate and removal
of the chloroform gave a yellow oil (15 g.) which
crystallised slowly. Recrystallisation from 60-80°
light petroleum gave white needles, m.p. 114°
(Found: C, 58.01; H, 8.25. $C_{11}H_{19}OPSi$ requires
C, 58.35, H, 8.4%).

Trimethyl-p-trimethylsilylphenylphosphonium iodide.-
Dimethyl-p-trimethylsilylphenylphosphine oxide (5.8 g.,
0.025 mole) was dissolved in benzene (40 ml.) and
added to lithium aluminium hydride (1.9 g., 0.05
mole) in di-butyl ether (40 ml.). The slurry was
stirred and refluxed for 3 hr. under nitrogen, cooled,
and treated with aqueous sodium hydroxide. The
organic layer was filtered under an atmosphere of
nitrogen and the solvent removed to give an oil
which was dissolved in benzene (40 ml.) and methyl
iodide was added. The crystals (5 g.) which formed

immediately were filtered off and recrystallised from 60-80° light petroleum/chloroform, to give white crystals, m.p. 183-184° (Found: C, 40.66; H, 6.26 $C_{12}H_{22}IPSi$ requires C, 40.9; H, 6.25%).

Trimethyl-p-trimethylsilylphenylphosphonium iodide was converted to the corresponding phosphonium hydroxide by boiling in aqueous solution with silver oxide. The solution was filtered and the water removed on the rotary evaporator to give an oil which was dissolved in absolute ethanol and the ethanol removed. Repetition of this process 10 times gave a white, hygroscopic, crystalline solid. Cleavage reactions were carried out on this material without it's being further purified.

Trimethyl-m-trimethylsilylphenylphosphonium iodide.-
(a) m-Trimethylsilylphenylphosphonic acid chloride (2.8 g., 0.011 mole) was added to the Grignard reagent from methyl iodide (7.1 g., 0.05 mole) and magnesium (1.2 g., 0.05 g.-atom) in ether (30 ml.). The mixture was then refluxed and stirred for 1 hr. Working up in the usual way gave 2 g. of an oil which would not crystallise. Distillation of this gave 1.5 g. of a viscous liquid, b.p. 150-160°/0.5-0.8 mm., which crystallised to give a low-melting solid, m.p. 38-40°.

The spectrum of this compound indicated that it was
dimethyl-m-trimethylsilylphenylphosphine oxide.

(b) Crude dimethyl-m-trimethylsilylphenylphosphine
oxide (1.5 g.) was dissolved in benzene (10 ml.) and
added to lithium aluminium hydride (0.9 g., 0.025 mole)
in dibutyl ether (10 ml.). The mixture was refluxed
and stirred, under dry nitrogen, for 3 hr. Ethyl
acetate was then added, to destroy excess lithium
aluminium hydride, followed by $\underline{N}$ hydrochloric acid.
The organic layer was quickly separated, filtered and
dried over anhydrous sodium sulphate. The solvent was
removed on a rotary evaporator to give an oil, which
was dissolved in benzene (4 ml.) and treated with
methyl iodide (2 g.). Crystals which immediately
separated were filtered off and one recrystallisation
from ethyl acetate gave 0.5 g. of trimethyl-m-trimeth-
ylsilylphenylphosphonium iodide, m.p. 173° (Found: C,
40.75; H, 6.41%).

The attempted conversion of this compound to
the phosphonium hydroxide led to complete loss of the
product.

3. The Preparation of some Benzylsilicon Compounds
containing Phosphorus.

(a) Preparation of organo-silicon compounds.

p-Chlorobenzyltrimethylsilane.- The Grignard reagent
from p-chlorobenzylchloride (177 g., 1.1 mole) and
magnesium (25 g., 1.1 g.-atom) was prepared in
anhydrous ether (800 ml.). To this was added
trimethylchlorosilane (108 g., 1.0 mole) in ether
(200 ml.) and the mixture was refluxed for 8 hr.
Working up in the usual way and fractionation, after
removal of the ether, gave 134 g. (70%) of p-chloro-
benzyltrimethylsilane, b.p. 102-102.5°/15 mm., n_D^{25}
1.5098 (lit.,[122] 231-232°, n_D^{12} 1.5154).

m-Chlorobenzyltrimethylsilane.-
(i) m-Chlorobenzylbromide was prepared by adding
bromine (180 g., 1.43 mole) to refluxing m-chloro-
toluene (180 g., 1.43 mole) over 3.5 hr. in an
apparatus illuminated with a 150 watt electric light
bulb. The mixture was then refluxed for a further
3 hr. Distillation gave 230 g. (78%) of m- chloro-
benzylbromide, b.p. 90°/8 mm. (lit.,[123] b.p. 109°/10mm.).
(ii) m-Chlorobenzyltrimethylsilane was prepared as
for p-chlorobenzyltrimethylsilane in 70% yield, b.p.

96-98°/10 mm., n_D^{20} 1.5109 (lit.,[122] 226-228°, n_D^{20} 1.5108).

(b) The preparation of benzylsilicon compounds containing phosphorus.

Diethyl p-trimethylsilylmethylphosphonate.- The Grignard reagent from p-chlorobenzyltrimethylsilane (99.2 g., 0.5 mole) and magnesium (12.15 g., 0.5 g.-atom) was prepared in refluxing THF, under nitrogen. (The halide was added over 1.5 hr. and the mixture was refluxed for a further 5 hr. The solution of the Grignard reagent was filtered into a dropping funnel and then added slowly to diethylphosphorochloridate (77.4 g., 0.45 mole) in ether (200 ml.), the reaction mixture being kept below 0°C. After the addition the reaction mixture was allowed to warm up to room temperature. Working up in the usual way gave 49 g. (36%) of diethyl p-trimethylsilylmethylphenylphosphonate, b.p. 134°/0.2 mm., n_D^{25} 1.4955 (Found: C, 55.33; H, 8.40. $C_{14}H_{25}O_3PSi$ requires C, 55.9; H, 8.33%).

Similarly prepared was:
Diethyl m-trimethylsilylmethylphenylphosphonate.- 56%

yield, b.p, 160-161°/3.0 mm., n_D^{25} 1.4942 (Found:

55.66; H, 8.21%).

p-Trimethylsilylmethylphenylphosphonic acid chloride.-

Diethyl p-trimethylsilylmethylphenylphosphonate (49.5

g., 0.15 mole) and phosphorus pentachloride (62.4 g.,

0.3 mole) were refluxed together for 4 hr. Distill-

ation, after removal of phosphorus oxychloride, gave

34 g. (81%) of a liquid, b.p. 136-138°/0.5 mm. This

material was assumed to be p-trimethylsilylmethyl-

phenylphosphonic acid chloride and was used in

subsequent preparations.

Similarly prepared was:

m-Trimethylsilylmethylphenylphosphonic acid chloride.-

86% yield, b.p. 119-122°/0.7 mm.

p-Trimethylsilylmethylphenylphosphonic acid.-

p-Trimethylsilylmethylphenylphosphonic acid chloride

(5 g.) was dissolved in acetone and 2N sodium

hydroxide was added until a clear solution was obtained.

The solution was then acidified with dilute hydro-

chloric acid and the precipitated acid extracted into

ether. Removal of the ether and recrystallisation of

the white solid gave p-trimethylsilylmethylphenyl-

phosphonic acid (3.9 g., 90%), m.p. 178° (Found:

C, 48.85; H, 7.05. $C_{10}H_{17}OPSi$ requires C, 49.15; H, 6.96%).

Similarly prepared was:

m-Trimethylsilylmethylphenylphosphonic acid.- 80% yield, m.p. 133°(Found: C, 49.05; H, 7.05%).

Diphenyl-p-trimethylsilylmethylphenylphosphine oxide.- p-Trimethylsilylmethylphenylphosphonic acid chloride (6.5 g., 0.022 mole) in ether was added to the Grignard reagent prepared from bromobenzene (7.85 g., 0.05 mole) and magnesium (1.2 g., 0.05 g.-atom) in ether (50 ml.) and the mixture was refluxed for 5 hr. Removal of the organic layer, after working up in the usual way, and evaporation of the ether gave 6 g. of a yellow solid. Recrystallisation from 60-80° light petroleum/ ethanol gave 5 g. (62%) of diphenyl-p-trimethylsilyl- methylphenylphosphine oxide, m.p. 151-152° (Found: C, 72.91; H, 6.80. $C_{22}H_{24}OPSi$ requires C, 72.7; H, 6.62%).

Similarly prepared was:
Diphenyl-m-trimethylsilylmethylphenylphosphine oxide.- The oil obtained would not crystallise and was distilled to give 6.5 g. (80%) of diphenyl-m-trimethyl-

silylmethylphenylphosphine oxide, b.p. 215-218°/0.1
mm. (Found: C, 72.47; H, 6.68%).

Dimethyl-p-trimethylsilylmethylphenylphosphine oxide.-
The Grignard reagent from methyl iodide (35.5 g., 0.25
mole) and magnesium (6.07 g., 0.25 g.-atom) was
prepared in ether (200 ml.). To this was added
p-trimethylsilylmethylphenylphosphonic acid chloride
(27.9 g., 0.1 mole) in ether (75 ml.) and the mixture
was refluxed for 5 hr. Working up in the usual way
gave a yellow solid which, on recrystallisation from
60-80° light petroleum gave 13.2 g. (55%) of dimethyl-
p-trimethylsilylmethylphosphine oxide, m.p. 134°
(Found: C, 60.08; H, 8.63. $C_{12}H_{21}OPSi$ requires C,
60.15; H, 8.75%).

Similarly prepared was:
Dimethyl-m-trimethylsilylmethylphenylphosphine oxide.-
The oil obtained, after working up in the usual way,
could not be crystallised and was distilled at
reduced pressure, b.p. 132°/0.07 mm., to give 10.2 g.
(75%) of an oil, which slowly crystallised on standing,
m.p. 35-38°. (Found: C, 60.00; H, 8.54%).

Trimethyl-p-trimethylsilylmethylphenylphosphonium
iodide.- Dimethyl-p-trimethylsilylmethylphenylphos-
phine oxide (7.2 g., 0.03 mole) was dissolved in

benzene (40 ml.) and added to lithium aluminium

hydride (2.28 g., 0.06 mole) in dibutyl ether (40 ml.).

The slurry was stirred and refluxed for 3 hr. Excess

lithium aluminium hydride was destroyed with ethyl

acetate and the mixture was poured onto ice/hydrochloric

acid (2$\underline{N}$). The aqueous and organic phases were

quickly separated and the organic layer filtered off

and dried over anhydrous sodium sulphate. The solvent

was removed on a rotary evaporator and the oil

remaining, assumed to be dimethyl-p-trimethylsilylmethyl-

phenylphosphine, was dissolved in benzene (40 ml.).

To this solution was added methyl iodide (10 ml.) in

benzene (20 ml.). An immediate reaction occurred

and a white solid was precipitated, which on recryst-

allisation from ethyl acetate gave 8.0 g. (73%) of

trimethyl-p-trimethylsilylmethylphenylphosphonium

iodide, m.p. 186°. (Found: C, 42.6; H, 6.71.

$C_{13}H_{24}IPSi$ requires C, 42.5; H, 6.61%).

Similarly prepared was:

Trimethyl-m-trimethylsilylmethylphenylphosphonium

iodide.- 80% yield, m.p. 160-162° (Found: C, 42.75;

H, 6.52%).

4. Cleavage of Arylsilanes.

Compounds and materials used for kinetic studies.

Arylsilanes.

Liquid arylsilanes were purified by fractionation through a 100 cm. Vigreux column. Solids were recrystallised several times until a constant melting point was obtained.

Acetic acid.

"Analar" acetic acid was purified by the method of Orton and Bradfield.[124] Acetic acid (2.5 1.) was refluxed with chromium trioxide (60 g.) for 2 hr., followed by distillation through a 70 cm. glass-helix-packed fractionating column. The first 200 ml. of distillate were discarded and the remainder collected and used for the kinetic studies.

Sulphuric acid.

Reagent grade sulphuric acid was used without further treatment. Sulphuric acid solutions of various concentration (16.3 $\underline{M}$, 11.7 $\underline{M}$ and 9.9 $\underline{M}$) were prepared by diluting 18.4 $\underline{M}$ sulphuric acid with deionized water and determined by titration against standard borax.

Fig. I Spectra of (a) p-Trimethylsilylphenylphosphonic acid
(b) Phenylphosphonic acid

λ (mμ)
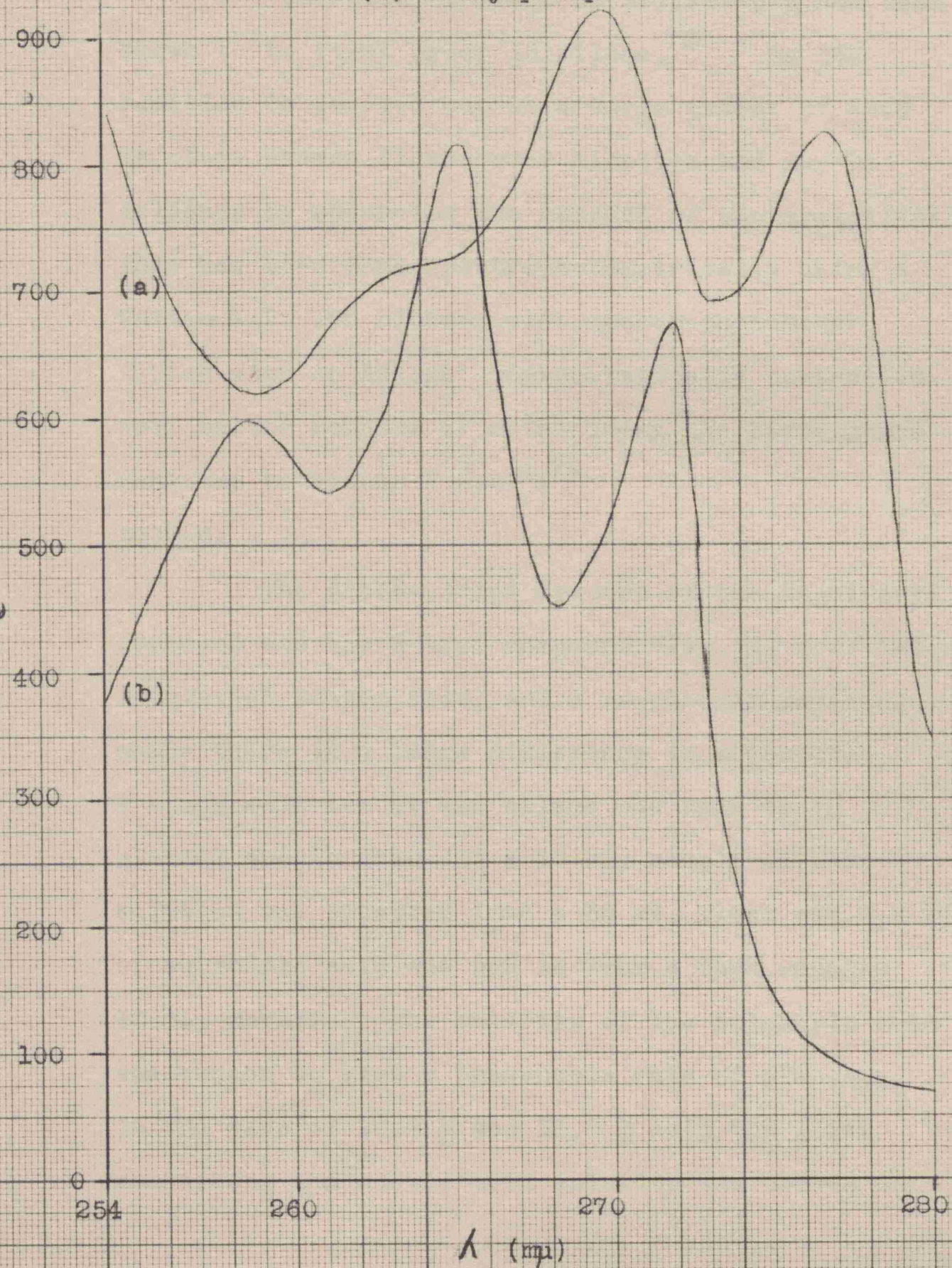
Kinetic measurements.

The acid cleavage of arylsilanes has been
shown to be first order in silane.[75]   As the
reaction is carried out in a large excess of acid
it obeys pseudo first-order kinetics and may be
followed by observing the removal of the arylsilane.
This has been done spectrophotometrically using a
Unicam S.P. 500 ultra-violet spectrophotometer
fitted with an Adkins' thermostatically controlled
cell holder capable of maintaining the temperature
constant to within ± 0.05°.[79]

Method.

The ultra-violet spectra of the Me_3Si-aryl
compound and the H-aryl compound (fig. I) were taken
in glacial acetic acid, and a wavelength selected
where there is a large difference in absorption.
A stock solution of the silane was made up in
glacial acetic acid and a 10 ml. sample of this
solution was pipetted into a 50 ml. flask and 7.5 ml.
of sulphuric acid was run in from a fast running
10 ml. burette. The molarity of the sulphuric acid
was chosen to give a reasonable rate of cleavage.
In the case of 18.4 M and 16.3 M acid the flask
containing the acetic acid solution was cooled in

ice-water, during the addition. After the air

bubbles in the reaction medium had dispersed, a

2.5 ml. sample was transferred to 1 cm. stoppered

cell, which was then placed in the cell holder.

The fall in optical density was measured, a water

blank being used as reference. Readings were

taken up to 80% reaction and infinity values taken

after ten "half lives". When this time exceeded

ten hours, infinity values were determined by

completing the reaction in sealed tubes, in a

water bath at 70°.

Calculation of rate constants.

For a first order reaction

$$\frac{dx}{dt} = k_1(a-x) \qquad (1)$$

where k_1 is the rate constant of the reaction,

a is the initial concentration of the reactant

and x is the amount reacted after time t.

Integration between $t=0$ and $t=t$ gives:

$$\log \frac{a}{a-x} = k_1 t \qquad (2)$$

The optical density of a solution is proportional

to the concentration of the compounds in that

solution at a specified wavelength (Beer's Law).

Hence:

$$\log\frac{a}{a-x} = \log\frac{D_0 - D_\infty}{D_t - D_\infty} = k_1 t \qquad (3)$$

and so

$$t = \frac{-2.303}{k_1} \log_{10}(D_t - D_\infty) + 2.303 \log_{10}(D_0 - D_\infty) \qquad (4)$$

where D_0 = optical density at time, $t = 0$

D_t = optical density at time, $t = t$

D_∞ = optical density at time, $t = \infty$

Thus, by plotting t against $\log_{10}D_t - D_\infty$, a straight line of slope $\dfrac{-2.303}{k_1}$ is obtained and

k = 2.303 x gradient.

All rate constants given in this work have been determined graphically by this method. In most cases duplicate determinations agreed within 0.5% and in all cases within 1.5%.

In the following tables a selection of the experimental values of D_t and t is given, observed during each run, together with the temperature of the block, the wavelength at which the run was followed and the molarity of the added sulphuric acid used.

The first-order plot for p-trimethyl-

Fig. II The cleavage of p-trimethylsilylphenylphosphonic acid

18.4M H₂SO₄   276.5 mμ   50°
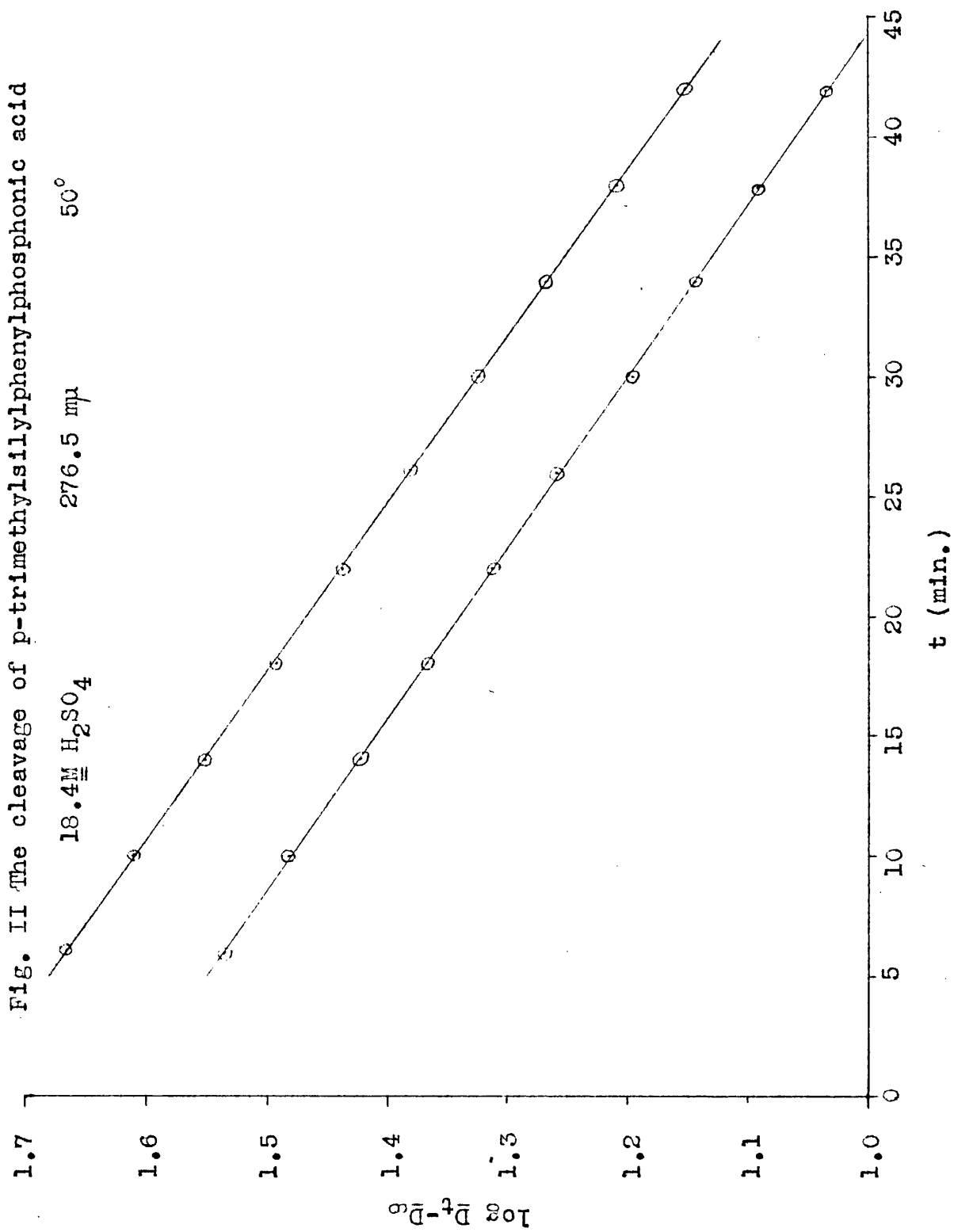
silylphenylphosphonic acid is given in fig. II.

Diphenyl-p-trimethylsilylphenylphosphine oxide

18.4$\underline{M}$ H_2SO_4 276.5 mμ 50°

t(min.)	30	50	90	120	140	180	∞
D_t	0.629	0.588	0.522	0.482	0.459	0.422	0.290

$$\underline{k}_1 = 6.33 \times 10^{-3} \text{ min.}^{-1}$$

t(min.)	20	72	100	140	170	200	∞
D_t	0.628	0.536	0.494	0.450	0.422	0.400	0.294

$$\underline{k}_1 = 6.36 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k}_1 = \underline{6.35 \times 10^{-3} \text{ min.}^{-1}}$$

Dimethyl-p-trimethylsilylphenylphosphine oxide

18.4$\underline{M}$ H_2SO_4 276.5 mμ 50°

t(min.)	10	50	80	100	150	160	∞
D_t	0.749	0.619	0.553	0.520	0.459	0.450	0.365

$$\underline{k}_1 = 9.39 \times 10^{-3} \text{ min.}^{-1}$$

t(min.)	10	30	50	60	80	140	∞
D_t	0.749	0.678	0.619	0.595	0.552	0.465	0.362

$$k_1 = 9.48 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k}_1 = \underline{9.44 \times 10^{-3} \text{ min.}^{-1}}$$

Trimethyl-p-trimethylsilylphenylphosphonium hydroxide.

18.4 $\underline{M}$ H_2SO_4 277.5 mμ 50 ^{o}.

t (min.)	30	50	80	100	125	160	∞
$\underline{D}_t$	0.508	0.442	0.371	0.333	0.297	0.261	0.185

$$\underline{k}_1 = 11.02 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)	10	30	70	100	120	140	∞
$\underline{D}_t$	0.623	0.540	0.422	0.358	0.327	0.302	0.284

$$\underline{k}_1 = 11.03 \times 10^{-3} \text{ min.}^{-1}$$

Mean $\underline{k}_1$ = $\underline{11.02 \times 10^{-3} \text{ min.}^{-1}}$

p-Nitrophenyltrimethylsilane.

18.4 $\underline{M}$ H_2SO_4 335 mμ 50 ^{c}.

t (min.)	5	20	35	50	65	80	∞
$\underline{D}_t$	0.518	0.470	0.438	0.410	0.384	0.364	0.273

$$\underline{k}_1 = 13.2 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)	10	20	40	50	65	80	∞
$\underline{D}_t$	0.495	0.466	0.422	0.403	0.382	0.361	0.275

$$\underline{k}_1 = 13.5 \times 10^{-3} \text{ min.}^{-1}$$

Mean $\underline{k}_1$ = $\underline{13.4 \times 10^{-3} \text{ min.}^{-1}}$

16.3 $\underline{M}$ H_2SO_4 355 mμ 50 ^{o}.

t (min.)	0	60	150	300	360	450	∞ *
$\underline{D}_t$	0.501	0.462	0.419	0.365	0.349	0.329	0.263

$$\underline{k}_1 = \underline{2.86 \times 10^{-3} \text{ min.}^{-1}}$$

t (min.)   0   60   120   210   270   480 ∞ *

$\underline{D}_t$ 0.498 0.460 0.429 0.390 0.370 0.321 0.262

$$\underline{k}_1 = 2.90 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k}_1 = \underline{2.88 \times 10^{-3} \text{ min.}^{-1}}$$

Trimethyl-p-trimethylphenylammonium hydroxide.

18.4 $\underline{\underline{M}}$ H_2SO_4 269.0 mμ 50°.

t (min.)   6   10   18   22   34   40 ∞

$\underline{D}_t$ 0.711 0.659 0.578 0.542 0.463 0.432 0.299

$$\underline{k}_1 = 33.05 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)   4   10   14   20   24   36 ∞

$\underline{D}_t$ 0.709 0.641 0.604 0.557 0.529 0.468 0.343

$$\underline{k}_1 = 33.35 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k}_1 = \underline{33.2 \times 10^{-3} \text{ min.}^{-1}}$$

Diethyl p-trimethylsilylphenylphosphonate.

18.4 $\underline{\underline{M}}$ H_2SO_4 276.5 mμ 50°.

t (min.)   5   25   45   55   70   80 ∞

$\underline{D}_t$ 0.680 0.583 0.513 0.484 0.453 0.438 0.352

$$k_1 = 18.6 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)   5   15   25   45   65   75 ∞

$\underline{D}_t$ 0.698 0.642 0.595 0.526 0.478 0.458 0.365

$$\underline{k}_1 = 18.2 \times 10^{-3} \text{ min.}^{-1}$$

Mean k_1 = $\underline{18.4 \times 10^{-3} \text{ min.}^{-1}}$

p-Trimethylsilylphenylphosphonic acid.

18.4 $\underline{M}$ H_2SO_4 276.5 mμ 50°.

t (min.)	8	14	20	24	34	40	∞
D_t	0.832	0.755	0.689	0.660	0.584	0.550	0.398

k_1 = 33.1 $\times 10^{-3}$ min.$^{-1}$

t (min.)	8	16	20	24	32	48	∞
D_t	0.801	0.714	0.670	0.641	0.587	0.508	0.400

k_1 = 32.9 $\times 10^{-3}$ min.$^{-1}$

Mean k_1 = $\underline{33.0 \times 10^{-3} \text{ min.}^{-1}}$

Diphenyl-m-trimethylsilylphenylphosphine oxide.

18.4 $\underline{M}$ H_2SO_4 283 mμ 50°.

t (min.)	8	14	22	26	36	50	∞
D_t	0.589	0.539	0.487	0.468	0.432	0.402	0.367

k_1 = 43.9 $\times 10^{-3}$ min.$^{-1}$

t (min.)	6	12	24	28	34	44	∞
D_t	0.610	0.551	0.478	0.459	0.439	0.414	0.370

k_1 = 44.2 $\times 10^{-3}$ min.$^{-1}$

Mean k_1 = $\underline{44.0 \times 10^{-3} \text{ min.}^{-1}}$

Diethyl m-trimethylsilylphenylphosphonate.

18.4 $\underline{M}$ H_2SO_4 276.0 mμ 50°.

t (min.)   5   8   9   10   14   15   ∝

D_t 0.597 0.550 0.536   0.523   0.486   0.478 0.398

$$k_1 = 90.3 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)   6   9   13   15   16   18   ∝

D_t 0.578 0.537 0.494   0.479   0.472   0.460 0.400

$$k_1 = 89.8 \times 10^{-3} \text{ min.}^{-1}$$

Mean k_1 = $\underline{90.1 \times 10^{-3} \text{ min.}^{-1}}$

16.3 $\underline{\underline{M}}$ H_2SO_4 276 mμ   50°.

t (min.)   5   15   20   25   35   46   ∞

D_t 0.589 0.520 0.491   0.466   0.427   0.396 0.325

$$k_1 = 32.8 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)   10   15   30   35   40   50   ∞

D_t 0.590 0.552 0.475   0.455   0.440   0.415 0.351

$$k_1 = 32.6 \times 10^{-3} \text{ min.}^{-1}$$

Mean k_1 = $\underline{32.7 \times 10^{-3} \text{ min.}^{-1}}$

m-Trimethylsilylphenylphosphonic acid.

18.4 $\underline{\underline{M}}$ H_2SO_4 275.5 mμ   50°.

t (min.)   4   6   7   10   12   15   ∞

D_t 0.692 0.618 0.596   0.539   0.517   0.491 0.449

$$k_1 = 152.0 \times 10^{-3} \text{ min.}^{-1}$$

t (min.) $3\frac{1}{2}$ $6\frac{1}{2}$ $7\frac{1}{2}$ 9   12   15 ∞

$\underline{D}_t$ 0.731 0.628 0.603 0.572 0.525 0.499 0.449

$$\underline{k}_1 = 151.0 \times 10^{-3} \text{ min.}^{-1}$$

$$\underline{\text{Mean }} \underline{k}_1 = \underline{151.5 \times 10^{-3} \text{ min.}^{-1}}$$

16.3 $\underline{\underline{M}}$ H_2SO_4 275.5 mμ 50°.

t (min.)   6   10   18   21   30   38 ∞

$\underline{D}_t$ 0.743 0.690 0.605 0.580 0.522 0.488 0.405

$$\underline{k}_1 = \underline{44.0 \times 10^{-3} \text{ min.}^{-1}}$$

t (min.)   8   12   16   22   28   35 ∞

$\underline{D}_t$ 0.740 0.689 0.642 0.590 0.548 0.511 0.409

$$\underline{k}_1 = 43.9 \times 10^{-3} \text{ min.}^{-1}$$

$$\underline{\text{Mean }} \underline{k}_1 = \underline{43.9 \times 10^{-3} \text{ min.}^{-1}}$$

m-Trimethylsilylbenzotrifluoride.

16.3 $\underline{\underline{M}}$ H_2SO_4 272.0 mμ 50°.

t (min.)   7   8   9   10   14   16 ∞

D_t 0.506 0.488 0.470 0.455 0.404 0.384 0.275

$$\underline{k}_1 = 83.7 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)   7   8   9   13   15   16 ∞

$\underline{D}_t$ 0.508 0.493 0.476 0.418 0.398 0.389 0.280

$$\underline{k}_1 = 83.4 \times 10^{-3} \text{ min.}^{-1}$$

$$\underline{\text{Mean }} \underline{k}_1 = \underline{83.6 \times 10^{-3} \text{ min.}^{-1}}$$

11.7 $\underline{M}$ H_2SO_4 272.0 mμ 50^c.

t (min.)	0	90	150	242	360	420	∞ *
$\underline{D}_t$	0.655	0.578	0.532	0.470	0.406	0.379	0.125

$$\underline{k}_1 = 1.75 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)	10	90	150	240	300	390	∞ *
$\underline{D}_t$	0.638	0.574	0.530	0.469	0.434	0.387	0.115

$$\underline{k}_1 = 1.74 \times 10^{-3} \text{ min.}^{-1}$$

Mean $\underline{k}_1$ = $\underline{1.75 \times 10^{-3} \text{ min.}^{-1}}$

Diethyl-m-trimethylsilylphenylphosphate.

11.7 $\underline{M}$ H_2SO_4 276.0 mμ 50°.

t (min.)	25	40	55	85	125	150	∞
$\underline{D}_t$	0.710	0.642	0.580	0.477	0.370	0.321	0.091

$$\underline{k}_1 = 7.91 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)	10	35	55	90	120	150	∞
$\underline{D}_t$	0.825	0.691	0.605	0.480	0.396	0.332	0.095

$$\underline{k}_1 = 8.01 \times 10^{-3} \text{ min.}^{-1}$$

Mean $\underline{k}_1$ = $\underline{7.96 \times 10^{-3} \text{ min.}^{-1}}$

m-Chlorophenyltrimethylsilane.

11.7 $\underline{M}$ H_2SO_4 280.0 mμ 50°.

t (min.)	10	35	45	60	85	120	∞
$\underline{D}_t$	0.731	0.599	0.552	0.494	0.414	0.334	0.118

$$\underline{k}_1 \;=\; 9.65 \text{ x } 10^{-3} \text{ min.}^{-1}$$

t (min.)	20	30	50	85	100	130	∞
$\underline{D}_t$	0.685	0.634	0.541	0.420	0.380	0.315	0.122

$$\underline{k}_1 \;=\; 9.70 \text{ x } 10^{-3} \text{ min.}^{-1}$$

$$\underline{\text{Mean }} \underline{k}_1 \;=\; \underline{9.68 \text{ x } 10^{-3} \text{ min.}}^{-1}$$

9.9 $\underline{\underline{M}}$ H_2SO_4 280.0 mμ 50°.

t (min.)	0	80	160	220	340	440	∞ *
$\underline{D}_t$	0.670	0.585	0.514	0.470	0.395	0.344	0.145

$$\underline{k}_1 \;=\; 2.48 \text{ x } 10^{-3} \text{ min.}^{-1}$$

t (min.)	0	40	100	200	280	400	∞ *
$\underline{D}_t$	0.665	0.621	0.561	0.484	0.430	0.364	0.145

$$\underline{k}_1 \;=\; 2.42 \text{ x } 10^{-3} \text{ min.}^{-1}$$

$$\underline{\text{Mean }} \underline{k}_1 \;=\; \underline{2.45 \text{ x } 10^{-3} \text{ min.}}^{-1}$$

Diethyl m-trimethylsilylbenzylphosphonate.

9.9 $\underline{\underline{M}}$ H_2SO_4 264.0 mμ 50°.

t (min.)	6	14	20	26	40	46	∞
$\underline{D}_t$	0.662	0.603	0.570	0.543	0.498	0.485	0.431

$$\underline{k}_1 \;=\; 36.5 \text{ x } 10^{-3} \text{ min.}^{-1}$$

t (min.)	4	10	16	24	30	41	∞
$\underline{D}_t$	0.705	0.654	0.614	0.572	0.547	0.514	0.449

$$\underline{k}_1 = 36.8 \times 10^{-3} \text{ min.}^{-1}$$

$$\underline{\text{Mean } k}_1 = \underline{36.6 \times 10^{-3} \text{ min.}^{-1}}$$

m-Trimethylsilylbenzylphosphonic acid.

9.9 $\underline{\text{M}}$ H_2SO_4 \qquad 264.0 mμ \qquad 50°.

t (min.)	4	12	14	25	28	35	∞
$\underline{D}_t$	0.759	0.653	0.634	0.558	0.543	0.518	0.464

$$\underline{k}_1 = 54.8 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)	6	10	14	20	26	35	∞
$\underline{D}_t$	0.726	0.675	0.634	0.586	0.552	0.518	0.464

$$\underline{k}_1 = 54.6 \times 10^{-3} \text{ min.}^{-1}$$

$$\underline{\text{Mean } k}_1 = \underline{54.5 \times 10^{-3} \text{ min.}^{-1}}$$

Diethyl-p-trimethylsilylphenylphosphate.

9.9 $\underline{\text{M}}$ H_2SO_4 \qquad 273.0 mμ \qquad 50°.

t (min.)	5	7	12	14	20	22	∞
$\underline{D}_t$	0.657	0.624	0.552	0.530	0.477	0.463	0.358

$$\underline{k}_1 = 61.8 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)	6	8	13	22	26	28	∞
$\underline{D}_t$	0.646	0.613	0.545	0.466	0.442	0.433	0.358

$$\underline{k}_1 = 61.0 \times 10^{-3} \text{ min.}^{-1}$$

$$\underline{\text{Mean } k}_1 = \underline{61.4 \times 10^{-3} \text{ min.}^{-1}}$$

Diethyl p-trimethylsilylbenzylphosphonate.

9.9 $\underline{M}$ H_2SO_4 · · · · · · · 269.0 mμ · · · · · · · 50°.

t (min.)	5	9	10	14	15	20	∞
D_t	0.528	0.408	0.385	0.320	0.307	0.266	0.215

$$k_1 = 121.8 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)	6	8	9	11	13	15	∞
D_t	0.505	0.444	0.416	0.373	0.338	0.312	0.215

$$\underline{k_1} = 120.8 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k_1} = \underline{121.3 \times 10^{-3} \text{ min.}^{-1}}$$

p-Trimethylsilylbenzylphosphonic acid.

9.9 $\underline{M}$ H_2SO_4 · · · · · · · 269.0 mμ · · · · · · · 50°.

t (min.)	4	6	9	11	16	17	∞
D_t	0.576	0.488	0.384	0.339	0.262	0.253	0.183

$$\underline{k_1} = 134.1 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)	5	9	11	14	17	19	∞
D_t	0.523	0.384	0.336	0.285	0.251	0.236	0.183

$$\underline{k_1} = 134.1 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k_1} = \underline{134.1 \times 10^{-3} \text{ min.}^{-1}}$$

Phenyltrimethylsilane.

9.9 $\underline{M}$ H_2SO_4 · · · · · · · 271.5 mμ · · · · · · · 50°.

t (min.)	$5\frac{1}{2}$	$6\frac{1}{2}$	9	10	$11\frac{1}{2}$	12	∞
D_t	0.443	0.385	0.272	0.241	0.199	0.187	0.072

$$\underline{k}_1 \;=\; 176.0 \times 10^{-3} \text{ min.}^{-1}$$

t (min.)	5	6	$7\frac{1}{2}$	8	10	12	∞
$\underline{D}_t$	0.499	0.432	0.350	0.328	0.253	0.201	0.074

$$k_1 \;=\; 172.6 \times 10^{-3} \text{ min.}^{-1}$$

$$\underline{\text{Mean } \underline{k}_1 \;=\; 174.3 \times 10^{-3} \text{ min.}^{-1}}$$

* For runs marked thus, end points were determined in sealed tubes.

5. Cleavage of Benzylsilanes.

Compounds and materials used for kinetic studies.

Benzylsilanes.

Liquid benzylsilanes were purified by fractionation through a 100 cm. Vigreux column. Solids were recrystallised several times until a constant melting point was obtained.

Aqueous methanol.

Aqueous methanol (39 wt.%) was prepared from "Analar" grade methanol, which had been distilled in apparatus fitted with a soda-lime trap, and boiled deionized water. The solution was made up to the correct composition by adjusting the specific gravity to the value required for 39 wt.% aqueous methanol.[125] The solution was stored in tightly stoppered bottles.
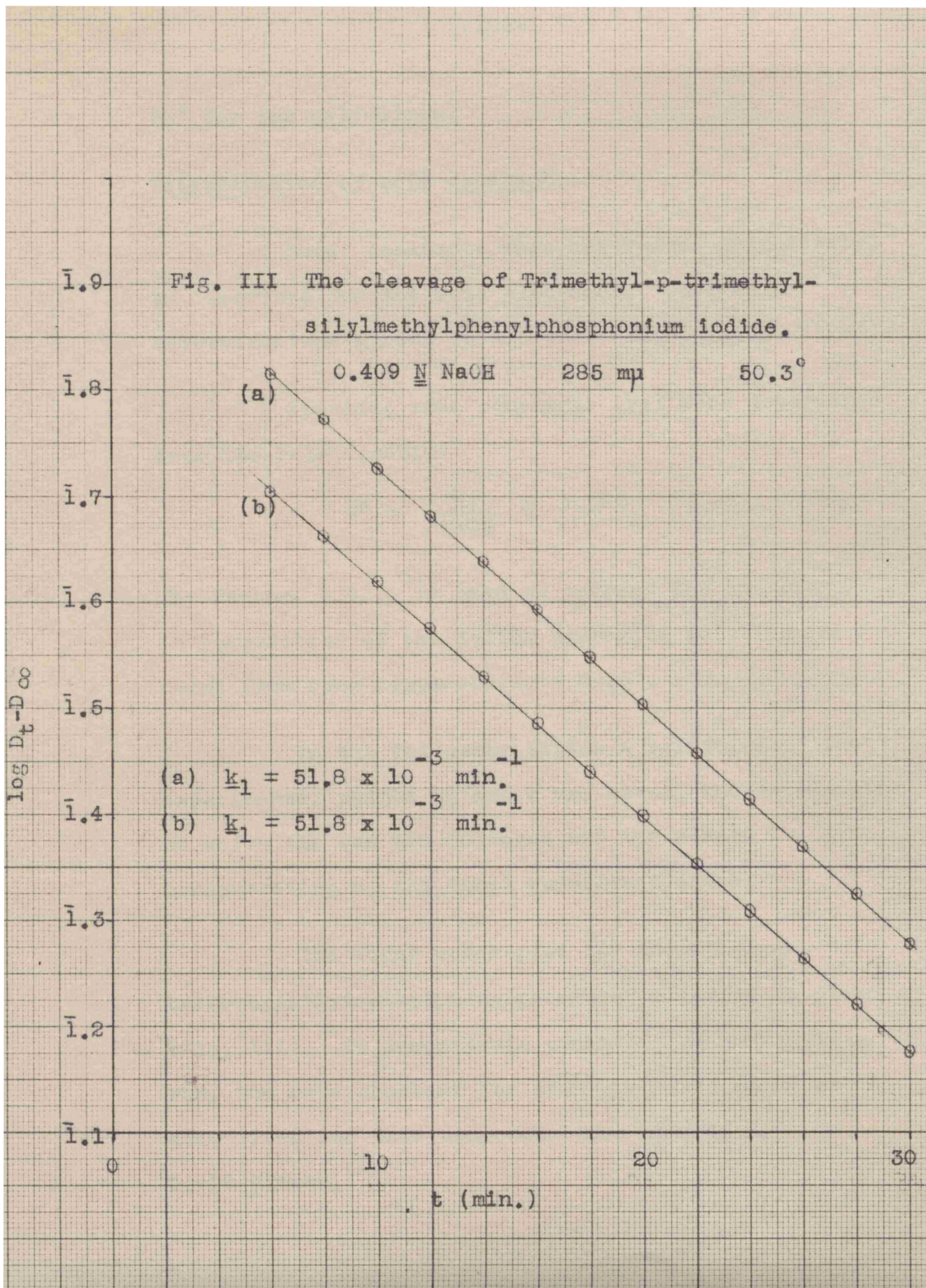
Aqueous methanolic sodium hydroxide.

Sufficient "Analar" sodium hydroxide was dissolved in 39 wt.% aqueous methanol to give an approximately 2$\underline{N}$ solution. Portions of this solution were diluted accurately, with aqueous methanol, to give the various concentrations required to cover the range of reactivities of the compounds studied.

The normalities of the solutions were deter-
mined by titration, after dilution, against 25 ml.
aliquots of 0.1N hydrochloric acid. This avoided
the necessity of calibration of pipettes for aqueous
methanolic media. The standardised solutions were
stored in tightly stoppered, graduated flasks. The
composition of the solutions was found not to vary
during the period of use.

Method.

The rate cleavage of benzylsilanes was
followed spectrophotometrically. A sample (5 ml.)
of a solution of the silane in 39 wt.% aqueous
methanol was pipetted into a flask and to this was
added 5 ml. of the required sodium hydroxide, the
same pipette being used for each sample. A portion of
this solution was transferred to a 1 cm. silica cell
which was then placed in the thermostated compartment
of the Unicam S.P. 500. The fall in optical density
was measured at one wavelength against an aqueous
methanol blank. The reaction was followed, in most
cases, for two half-lives, and the infinity value
was determined after ten half-lives. Where this time
exceeded 10 hr. a sample was transferred to a stoppered
pyrex conical flask and kept in a thermostat bath at

Fig. III The cleavage of Trimethyl-p-trimethyl-
silylmethylphenylphosphonium iodide.

0.409 $\underline{N}$ NaOH   285 mμ 50.3°

(a) $\underline{k}_1 = 51.8 \times 10^{-3}$ min.$^{-1}$
(b) $\underline{k}_1 = 51.8 \times 10^{-3}$ min.$^{-1}$

50° for ten half-lives.

Determination of rate constants.

Rate constants were determined graphically, as described for the acid cleavages. Duplicate determinations agreed in all cases within 1.5%.

Specific rate constants (ks) were determined from the relationship:

$$ks = \frac{k_1}{NaOH} \times 1.025$$

The factor, 1.025, is used to correct for the change in composition of the sodium hydroxide solution in going from room temperature to 50.3°.

In the following tables a selection of the experimental points D_t and t are given, the wavelength at which the run was followed and the alkali concentration of the final reaction mixture.

The first order plot for trimethyl-m-trimethylsilylmethylphenylphosphonium iodide is given (fig. III). To demonstrate constancy of k_1 within a run, the rate constant for each graphical point is also given for this compound, when cleaved in 0.409 N NaOH.

Trimethyl-p-trimethylsilylmethylphenylphosphonium
iodide

5.05×10^{-3} $\underline{N}$ NaOH   266 mμ 50.3°

t(min.)	6	9	14	17	26	30	∞
$\underline{D}_t$	0.642	0.569	0.472	0.426	0.331	0.303	0.200

$$\underline{k}_1 = 60.6 \times 10^{-3} \text{ min.}^{-1}$$

t(min.)	7	11	17	19	24	30	∞
$\underline{D}_t$	0.608	0.519	0.420	0.395	0.342	0.297	0.195

$$\underline{k}_1 = 60.4 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k}_1 = \underline{60.5 \times 10^{-3} \text{ min.}^{-1}}$$

$$\underline{k}_s = \underline{12.3 \text{ min.}^{-1} \text{ mole}^{-1}\text{l.}}$$

Diphenyl-p-trimethylsilylmethylphenylphosphine oxide

0.1027 $\underline{N}$ NaOH   266 mμ 50.3°

t(min.)	5	8	12	24	28	32	∞
$\underline{D}_t$	0.618	0.581	0.537	0.442	0.421	0.402	0.306

$$\underline{k}_1 = 43.6 \times 10^{-3} \text{ min.}^{-1}$$

t(min.)	4	8	16	18	22	26	∞
$\underline{D}_t$	0.647	0.592	0.511	0.494	0.464	0.440	0.312

$$\underline{k}_1 = 43.7 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k}_1 = \underline{43.7 \times 10^{-3} \text{ min.}^{-1}}$$

$$\underline{k}_s = \underline{4.36 \times 10^{-1} \text{ min.}^{-1} \text{ mole}^{-1}\text{l.}}$$

Diethyl p-trimethylsilylmethylphenylphosphonate

0.1027 $\underline{N}$ NaOH   266 mμ 50.3^c

t(min.)	0	4	16	22	26	31	∞
$\underline{D}_t$	0.918	0.879	0.791	0.759	0.741	0.722	0.629

$$\underline{k}_1 = 36.5 \times 10^{-3} \text{ min.}^{-1}$$

t(min.)	0	12	16	20	24	32	∞
$\underline{D}_t$	0.675	0.595	0.575	0.559	0.544	0.520	0.448

$$\underline{k}_1 = 36.1 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k}_1 = 36.3 \times 10^{-3} \text{ min.}^{-1}$$

$$\underline{k}_s = 3.62 \times 10^{-1} \text{ min.}^{-1} \text{ mole}^{-1}\text{l.}$$

Dimethyl-p-trimethylsilylmethylphenylphosphine oxide

0.1027 $\underline{N}$ NaOH   266 mμ 50.3^o

t(min.)	0	25	35	45	71	100	∞
$\underline{D}_t$	0.776	0.669	0.633	0.603	0.537	0.483	0.340

$$\underline{k}_1 = 11.2 \times 10^{-3} \text{ min.}^{-1}$$

t(min.)	0	15	40	55	70	90	∞
$\underline{D}_t$	0.754	0.689	0.602	0.561	0.527	0.490	0.341

$$\underline{k}_1 = 11.2 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k}_1 = 11.2 \times 10^{-3} \text{ min.}^{-1}$$

$$\underline{k}_s = 1.12 \times 10^{-1} \text{ min.}^{-1} \text{ mole}^{-1}\text{l.}$$

Trimethyl-m-trimethylsilylmethylphenylphosphonium iodide

0.409 $\underline{N}$ NaOH   285 mμ 50.3^c

t(min.)	9	11	15	19	26	30	∞
$\underline{D}_t$	0.538	0.493	0.419	0.358	0.278	0.245	0.096
$\underline{k}_1$	51.6	51.9	51.8	51.7	52.1	51.8	

$$\underline{k}_1 = 51.8 \times 10^{-3} \text{ min.}^{-1}$$

t(min.)	8	11	14	17	20	30	∞
$\underline{D}_t$	0.563	0.498	0.439	0.390	0.349	0.245	0.095
$\underline{k}_1$	52.5	51.8	51.9	51.8	51.6	51.8	

$$\underline{k}_1 = 51.8 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k}_1 = \underline{51.8 \times 10^{-3} \text{ min.}^{-1}}$$

$$\underline{k}_s = \underline{1.30 \times 10^{-1} \text{ min.}^{-1} \text{ mole}^{-1}\text{l.}}$$

1.027 $\underline{N}$ NaOH   285 mμ 50.3^c

t(min.)	6	8	12	14	16	20	∞
$\underline{D}_t$	0.524	0.443	0.328	0.285	0.255	0.210	0.142

$$\underline{k}_1 = 123.9 \times 10^{-3} \text{ min.}^{-1}$$

$$\underline{k}_s = \underline{1.235 \times 10^{-1} \text{ min.}^{-1} \text{ mole}^{-1}\text{l.}}$$

0.775 $\underline{N}$ NaOH   285 mμ 50.3^o

t(min.)	5	8	11	16	21	23	∞
$\underline{D}_t$	0.600	0.482	0.393	0.290	0.228	0.211	0.126

$$\underline{k}_1 = 123.9 \times 10^{-3} \text{ min.}^{-1}$$

$$\underline{k}_3 = \underline{1.235 \times 10^{-1} \text{ min.}^{-1} \text{ mole}^{-1} \text{l.}}$$

0.535 $\underline{N}$ NaOH   285 mμ 50.3°

t(min.)	5	8	11	14	19	25	∞
$\underline{D}_t$	0.625	0.531	0.457	0.396	0.316	0.251	0.117

$$\underline{k}_1 = 66.5 \times 10^{-3} \text{ min.}^{-1}$$

$$\underline{k}_3 = \underline{1.285 \times 10^{-1} \text{ min.}^{-1} \text{ mole}^{-1} \text{l.}}$$

0.204 $\underline{N}$ NaOH   285 mμ 50.3°

t(min.)	8	24	30	40	50	60	∞
$\underline{D}_t$	0.627	0.439	0.387	0.318	0.264	0.223	0.090

$$\underline{k}_1 = 26.8 \times 10^{-3} \text{ min.}^{-1}$$

$$\underline{k}_3 = \underline{1.345 \times 10^{-1} \text{ min.}^{-1} \text{ mole}^{-1} \text{l.}}$$

Diphenyl-m-trimethylsilylmethylphenylphosphine oxide

1.027 $\underline{N}$ NaOH   285 mμ 50.3°

t(min.)	20	40	55	75	86	100	∞
$\underline{D}_t$	0.788	0.741	0.712	0.678	0.659	0.640	0.461

$$\underline{k}_1 = 7.53 \times 10^{-3} \text{ min.}^{-1}$$

t(min.)	30	35	55	65	85	100	∞
$\underline{D}_t$	0.764	0.752	0.711	0.693	0.660	0.639	0.461

$$\underline{k}_1 = 7.55 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k}_1 = \underline{7.54 \times 10^{-3} \text{ min.}^{-1}}$$

$$\underline{k}_s = \underline{7.52 \times 10^{-3} \text{ min.}^{-1} \text{ mole}^{-1}\text{l.}}$$

Dimethyl-m-trimethylsilylmethylphenylphosphine oxide

1.027 $\underline{N}$ NaOH   278 mμ 50.3°

t(min.)	45	90	165	200	270	315	∞
$\underline{D}_t$	0.568	0.508	0.425	0.395	0.347	0.321	0.195

$$\underline{k}_1 = 4.02 \times 10^{-3} \text{ min.}^{-1}$$

t(min.)	30	60	121	240	300	360	∞
$\underline{D}_t$	0.558	0.518	0.444	0.346	0.311	0.282	0.185

$$\underline{k}_1 = 4.03 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k}_1 = \underline{4.02 \times 10^{-3} \text{ min.}^{-1}}$$

$$\underline{k}_s = \underline{4.01 \times 10^{-3} \text{ min.}^{-1} \text{ mole}^{-1}\text{l.}}$$

m-Trimethylsilylmethylbenzotrifluoride

1.027 $\underline{N}$ NaOH   279 mμ 50.3°

t(min.)	0	120	175	270	361	420	∞
$\underline{D}_t$	0.868	0.619	0.532	0.415	0.330	0.288	0.100

$$\underline{k}_1 = 3.30 \times 10^{-3} \text{ min.}^{-1}$$

t(min.)	0	60	152	240	322	405	∞
$\underline{D}_t$	0.875	0.738	0.578	0.459	0.376	0.312	0.110

$$\underline{k}_1 = 3.27 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k}_1 = \underline{3.28 \times 10^{-3} \text{ min.}^{-1}}$$

$$\underline{k}_s = \underline{3.27 \times 10^{-3} \text{ min.}^{-1} \text{ mole}^{-1}\text{l.}}$$

m-Chlorobenzyltrimethylsilane

1.027 $\underline{N}$ NaOH $\qquad$ 280 mμ $\qquad$ 50.3^c

t(min.)	0	64	150	210	300	420	∞
$\underline{D}_t$	0.685	0.623	0.550	0.504	0.448	0.385	0.145

$$\underline{k}_1 = 1.92 \times 10^{-3} \text{ min.}^{-1}$$

t(min.)	0	120	245	330	420	510	∞
$\underline{D}_t$	0.672	0.563	0.472	0.422	0.378	0.341	0.145

$$\underline{k}_1 = 1.94 \times 10^{-3} \text{ min.}^{-1}$$

$$\text{Mean } \underline{k}_1 = \underline{1.93 \times 10^{-3} \text{ min.}^{-1}}$$

$$\underline{k}_s = \underline{1.92 \times 10^{-3} \text{ min.}^{-1} \text{ mole}^{-1}\text{l.}}$$

Attempted cleavage of p-trimethylsilylmethylphenyl-phosphonic acid

(i) A sample (10 ml.) of a solution of $\underline{p}$-trimethyl-silylmethylphenylphosphonic acid (0.4 g./l.) in 39 wt.% aqueous methanol was pipetted into a conical flask. To this was added 10 ml. of 1.027 $\underline{N}$ sodium hydroxide in 39 wt.% aqueous methanol. The flask was immersed in a thermostat bath at 50° and samples (2.5 ml.) were withdrawn at 24 hr. intervals and the optical density of these measured against an aqueous methanol blank. No fall in optical density was observed over 120 hr.

(11) p-Trimethylsilylmethylphenylphosphonic acid

(1 g.) was dissolved in 2N aqueous alcoholic

sodium hydroxide solution. The mixture was refluxed

for 16 hr. after which it was acidified and extracted

with ether. Removal of the ether left a white,

crystalline solid (0.8 g.), the infrared spectrum

of which corresponded to that of p-trimethylsilyl-

methylphenylphosphonic acid. One recrystallisation

of this gave pure p-trimethylsilylmethylphenyl-

phosphonic acid, m.p. 176°.

Attempted cleavage of m-trimethylsilylmethylphenyl-
phosphonic acid

Similarly, no change in spectrum was observed when

a solution of m-trimethylsilylmethylphenylphosphonic

acid, in 2N aqueous alcoholic sodium hydroxide

solution was kept in a thermostat bath at 50°, over

96 hr.

Hydrolyses of diethyl phenylphosphonate

(i) An attempt was made to follow the hydrolyses

of diethyl phenylphosphonate in 1.027 N sodium

hydroxide solution at 50.3°. A sample (5 ml.)

of a solution of diethyl phenylphosphonate

(0.316 g./l.), in 39 wt.% aqueous methanol was

pipetted into a conical flask and to this was added

5 ml. of 1.027 $\underline{N}$ sodium hydroxide solution (in 39 wt.%

aqueous methanol). The fall in optical density $(\underline{D}_t)$

was followed over 10 hr.:

t(min.)	0	20	40	63	105	135	600
$\underline{D}_t$	0.609	0.593	0.576	0.558	0.531	0.519	0.495

(ii) A similar sample was treated with 0.1027 $\underline{N}$

sodium hydroxide solution. The optical density

of this fell from 0.604 to 0.592 in 10 hr.

6. Protonation of the Phosphoryl Bond

(a) Protonation of triphenylphosphine oxide in aqueous sulphuric acid

Triphenylphosphine oxide

A sample of triphenylphosphine oxide (Albright and Wilson (Mfg.) Ltd.) was recrystallised from 60-80° light petroleum until a constant melting point (153°) was obtained (lit.,[125] m.p. 152-153°).

Sulphuric acid solutions

Aqueous sulphuric acid solutions (10-80 wt.%) were prepared by diluting "Analar" concentrated sulphuric acid with deionised water. The exact composition of each solution was determined by accurate dilution of a weighed sample and titration of the resulting solution against standard sodium hydroxide solution (0.1$\underline{N}$) using screened methyl orange. The H_0 values for the solutions were derived from the data of Paul and Long.[108]

Spectra

Ultraviolet spectra were determined on the

Unicam S.P. 500 spectrophotometer, fitted with a
thermostated cell compartment, maintained at
$30 \pm 0.02°$.

Method

A stock solution of triphenylphosphine
oxide (0.0264 g.) was made up in acetone (50 ml.).
For each acid concentration a known weight of the
stock solution (ca. 0.5 ml.) was pipetted into a
conical flask and the acetone removed at the pump,
leaving a thin film of triphenylphosphine oxide
(ca. 2.5×10^{-4} g.) on the walls of the flask.
To this was added a known weight of sulphuric acid
solution (ca. 5 ml.), the exact volume of which
was calculated from published density data.
In this way the exact concentration (g./l.) of
triphenylphosphine oxide in the sulphuric acid
solution was calculated.

In most cases the triphenylphosphine
oxide film dissolved readily, but in the cases of
9.83 wt.% and 19.71 wt.% sulphuric acid solutions
the flask had to be warmed, by immersion in a water
bath at 50°, to effect complete solution.

Fig. IV The spectra of triphenylphosphine oxide in (a) 81.4;
(b) 68.7; (c) 53.1; (d) 42.2; (e) 19.7 wt.% aqueous
sulphuric acid solutions
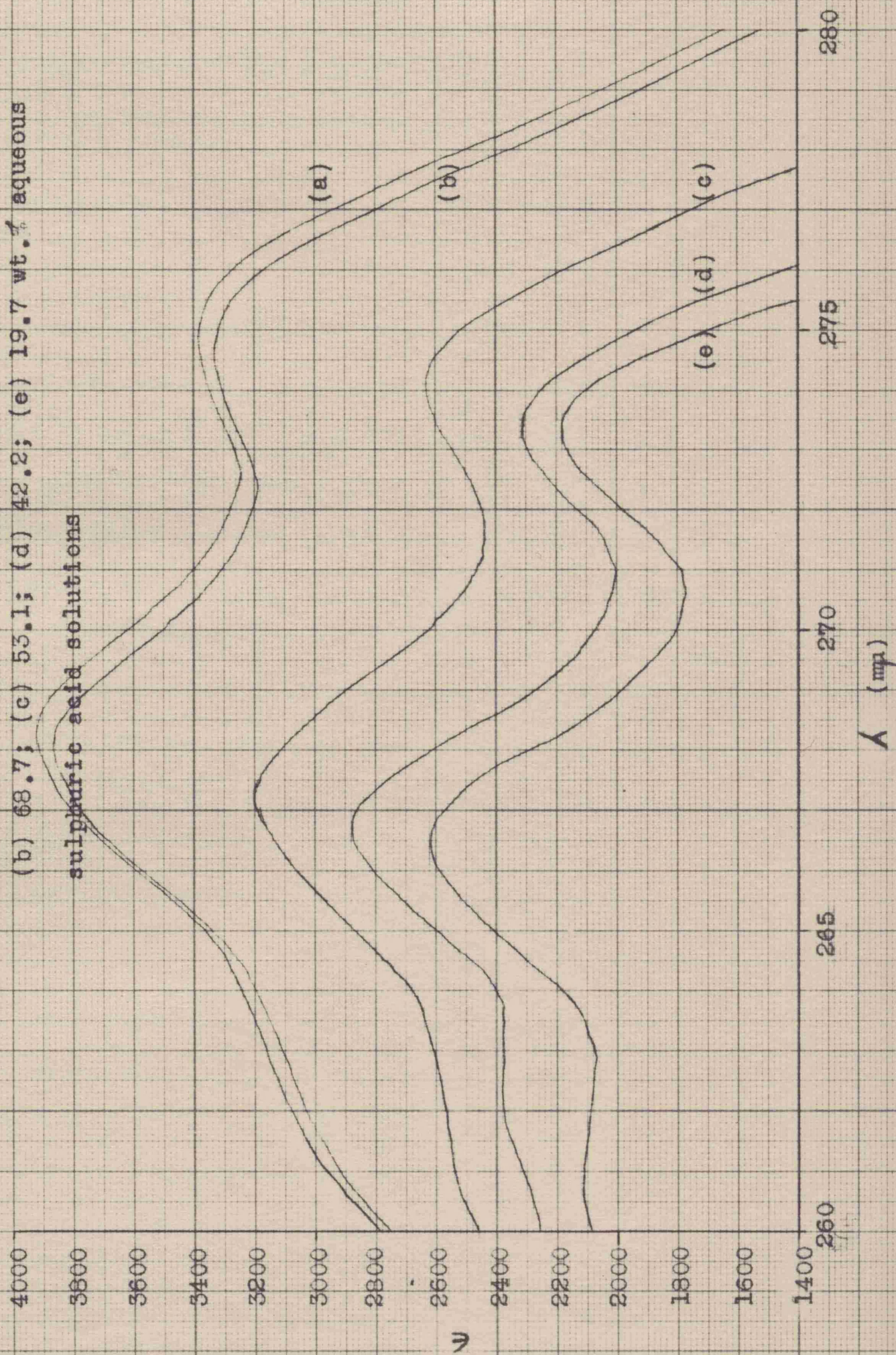
Table XIV. Extinction coefficients (ϵ) of triphenyl-
phosphine oxide in various solutions of
aqueous sulphuric acid

Sulphuric acid (wt.%)	H_o	268 mμ	274 mμ
81.4	-7.15	3907	3332
68.7	-5.5	3873	3278
62.5	-4.75	3732	3142
57.25	-4.17	3479	2916
53.1	-3.67	3137	2650
51.2	-3.50	3016	2560
49.25	-3.27	2899	2470
46.0	-2.95	2740	2365
42.2	-2.60	2590	2258
30.35	-1.72	2360	2120
19.71	-1.00	2273	2067

Fig. V Extinction coefficients at 268 mμ and 274 mμ against H_0
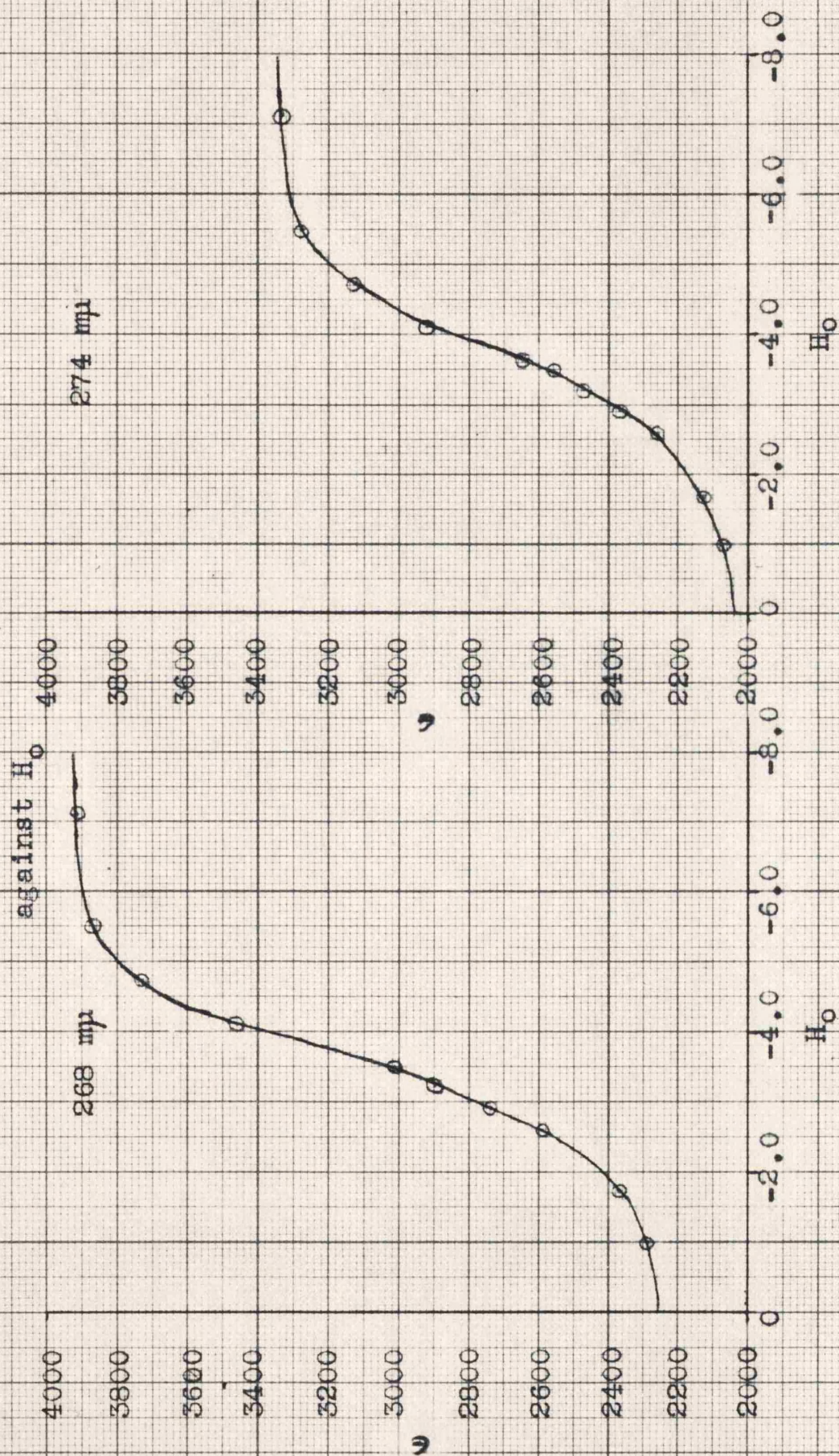
A sample (2.5 ml.) of the resulting solution
was transferred to a 1 cm. stoppered cell and the
spectrum measured against a blank of the same
sulphuric acid solution, over the range 255-280 mμ,
at 1 mμ intervals.

The extinction coefficient (ϵ) observed at
268 mμ and 274 mμ for various acid concentrations are
given in table XIV.

The spectra of triphenylphosphine oxide in
81.4%, 68.7%, 53.1%, 42.2% and 19.7% sulphuric acid
solutions are shown in fig. IV.

The sigmoid curves obtained by plotting
extinction coefficient at 268 mμ and 274 mμ versus
H_0 are given in fig. V.

(b) The protonation of triphenylphosphine oxide in
sulphuric acid-acetic acid mixtures

Triphenylphosphine oxide

Triphenylphosphine oxide was purified as
described in section 6 (a).

Glacial acetic acid

Glacial acetic acid was dried by distillation

Fig. VI   The spectra of triphenylphosphine oxide in glacial acetic acid-sulphuric acid mixtures
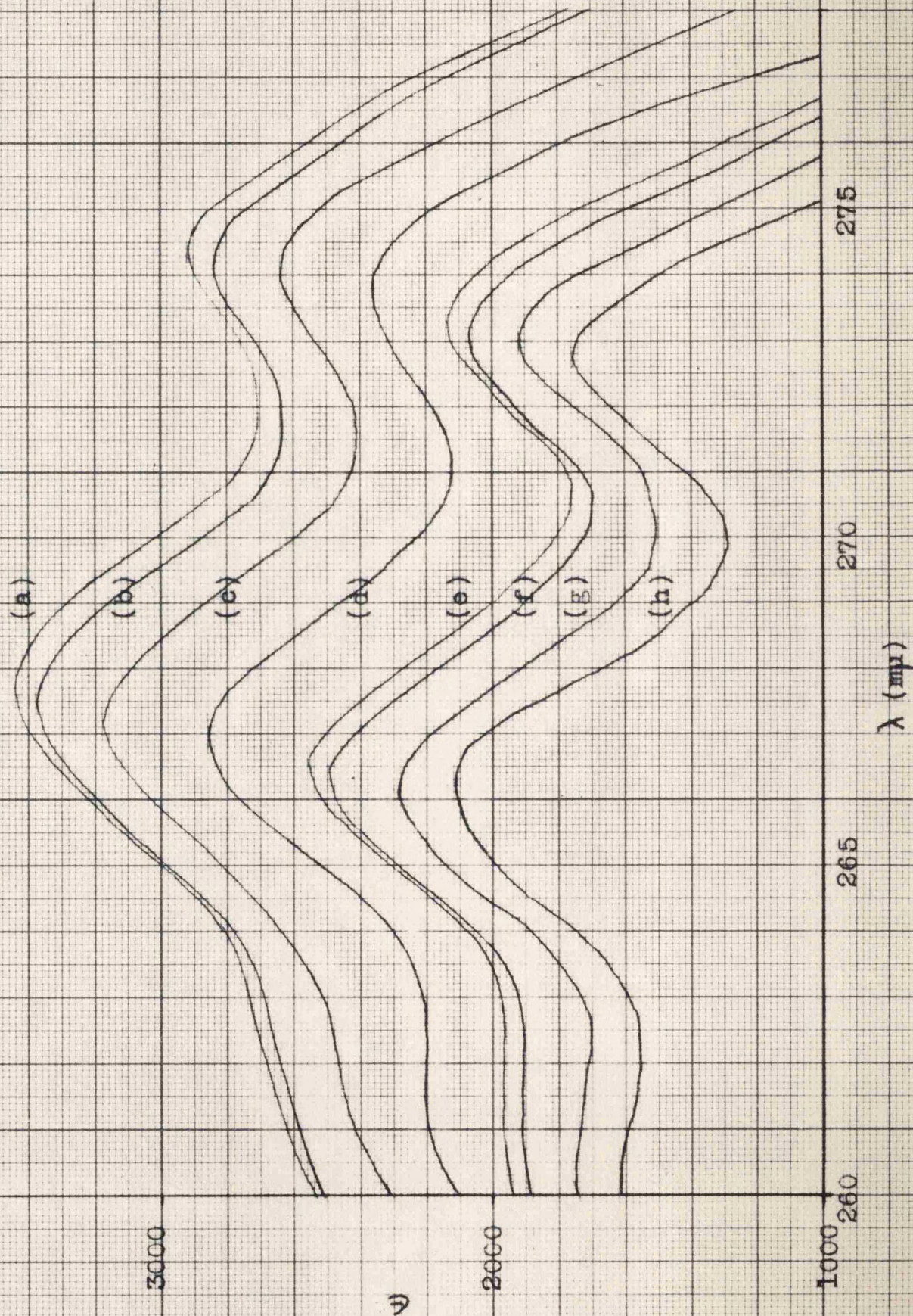
Fig. VII Extinction coefficient at (a) 268 mµ and (b) 274 mµ
versus wt.% sulphuric acid
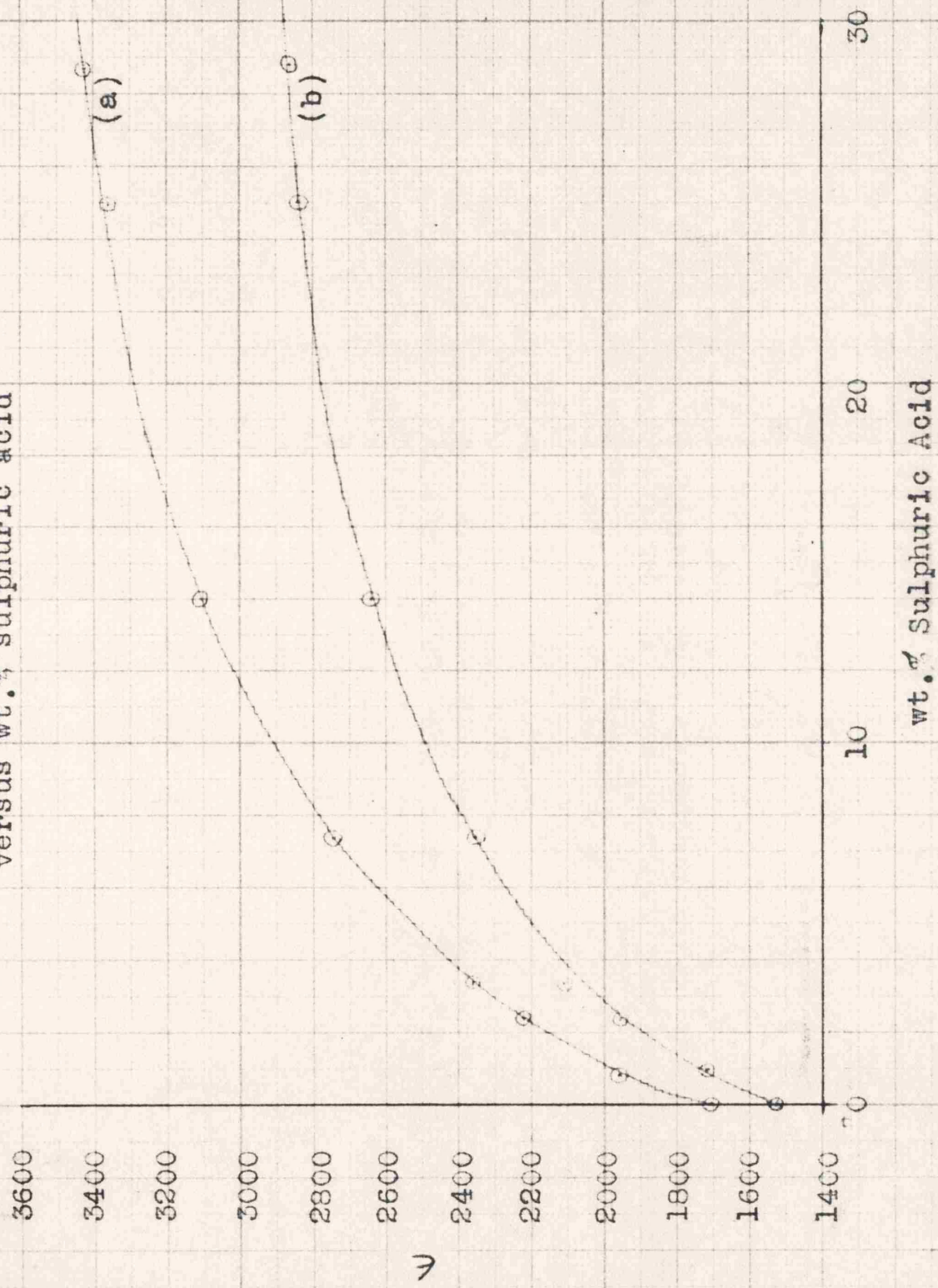
as described in section 4 (p. 89).

Sulphuric acid

The sample of 18.4$\underline{M}$ sulphuric acid used in the kinetic studies (section 4) was employed.

Method

A stock solution of triphenylphosphine oxide (0.088 g./l.) in glacial acetic acid was prepared. To a weighed sample (10 ml.) of this solution was added a known weight of concentrated sulphuric acid (18.4$\underline{M}$) and the spectrum of the mixture measured between 255 mμ and 280 mμ against a sulphuric acid-acetic acid blank of approximately the same concentration. The spectra of triphenylphosphine oxide in glacial acetic acid and in (a) 28.7; (b) 25.1; (c) 14.05; (d) 7.45; (e) 3.53; (f) 2.43; (g) 0.896; (h) 0.0 wt.% sulphuric acid are given in fig. VI. In fig. VII plots of the extinction coeffecient at 268 mμ and 274 mμ versus the sulphuric acid concentration (wt.%) are given.

PART II

The Preparation and Reactions of some Aliphatic

Phosphorus Compounds Containing Silicon

CHAPTER V

The Preparation and Properties of Silicon-containing

Aliphatic Phosphorus Compounds

The Preparation and Properties of Silicon-containing Aliphatic Phosphorus Compounds

Interest in organophosphorus compounds containing silicon has increased during the past ten years because of their importance in industrial application. Numerous references to such compounds have appeared in the patent literature, claiming their use as plasticisers, flame-proofing agents, lubricants or lubricant additives, insecticides, etc.[127,128,129]

The preparation of organophosphorus compounds containing silicon

(a) Compounds containing silicon-phosphorus linkages

Trimethylsilyldiphenylphosphine may be prepared by the action of diphenyl sodium phosphide on trimethylchlorosilane.[130]

$$Ph_2PNa + Me_3SiCl \longrightarrow Ph_2PSiMe_3 + NaCl$$
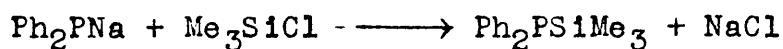
The reaction between lithium phosphides and chlorotrialkylsilanes has also been described and affords a useful general method for the production of trialkylsilylphosphines.[142]

$$LiPH_2 + Me_3SiCl \longrightarrow Me_3SiPH_2 + LiCl$$

The Michaelis-Arbusov reaction has been successfully applied to the preparation of alkylsilylphosphonates. Thus, heating triethylphosphite with triethylbromosilane gave diethyl trimethylsilylphosphonate.[131]

$$(EtO)_3P + BrSiEt_3 \longrightarrow EtBr + Et_3SiPO(OEt)_2$$
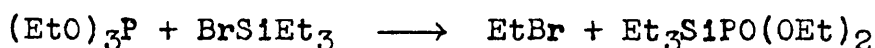
Similarly, triethoxybromosilane with triethylphosphite gave diethyl triethoxysilylphosphonate.

The Michaelis reaction; the reaction of alkyl halides with sodio-derivatives of dialkylphosphonates, has been used with alkyl-substituted silicon halides.[132,133]

$$(R'O)_2PONa + R_3SiCl \longrightarrow (R'O)_2OPSiR_3 + NaCl$$

Newlands[134] has reported the reaction of triphenylsilyllithium with dibenzylphosphorochloridate.

$$Ph_3PhI + (BzO)_2POCl \longrightarrow Ph_3SiPO(OBz)_2$$

(b) Compounds containing silicon-carbon-phosphorus linkages

Seyferth[135] has prepared tris(trimethylsilylmethyl)phosphine from phosphorus tribromide and the Grignard reagent from chloromethyltrimethylsilane.

$$3Me_3SiCH_2MgCl + PBr_3 \longrightarrow (Me_3SiCH_2)_3P$$
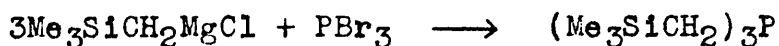
As alkylphosphines are highly susceptible

to oxidation, tris(trimethylsilylmethyl)phosphine oxide was also isolated from the reaction mixture.

The Michaelis-Arbusov reaction has been used for the preparation of diethyl trimethyl-silylmethylphosphonate and diethyl pentamethyl-siloxanylphosphonate.[136]

$$(EtO)_3P + Me_3SiCH_2Cl \longrightarrow Me_3SiCH_2PO(OEt)_2 + EtCl$$

$$(EtO)_3P + Me_3SiOSiMe_2CH_2Cl \longrightarrow Me_3SiOSiMe_2CH_2PO(OEt)_2 + EtCl$$
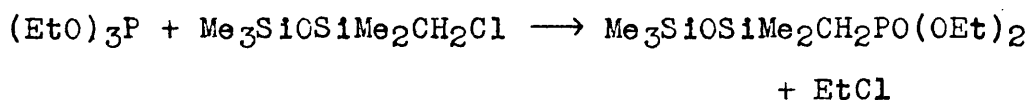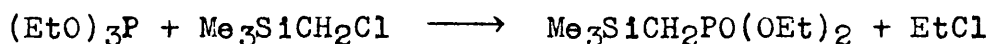
Similar products have also been obtained using the Michaelis reaction.[133]

$$Me_3SiOSiMe_2CH_2Br + (n-BuO)_2PONa \longrightarrow$$
$$Me_3SiOSiMe_2CH_2PO(OBu^n)_2 + NaBr$$

$$Me_3SiCH_2Br + (n-BuO)_2PONa \longrightarrow$$
$$Me_3SiCH_2PO(OnBu^n)_2 + NaBr$$
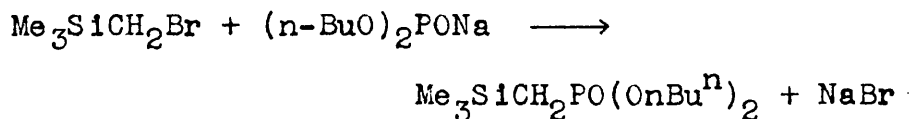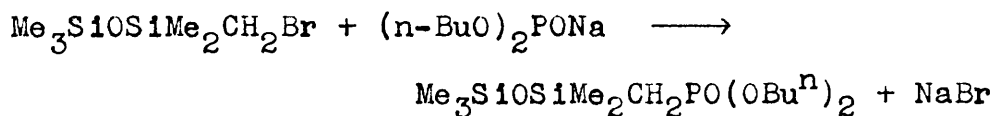
Alkylphosphonic dichloride may be prepared by the method of oxidative phosphonation.[137]

$$RH + PCl_3 + \tfrac{1}{2}O_2 \longrightarrow RPOCl_2 + HCl$$

Gilbert and Precopio found that tetramethylsilane

reacted in this way to give trimethylsilylmethyl-
phosphonic dichloride.[136] Similarly, Cherneyshev
and Petrov used this reaction to prepare silicon-
substituted derivatives of ethylphosphonic
dichloride:[138]

$$EtSiCl_3 + PCl_3 + \tfrac{1}{2}O_2 \longrightarrow Cl_3SiCH_2CH_2POCl_2$$

Linville[128] and also Marsden[129] have
prepared dialkyl silicon-containing ethylphos-
phonates by the free radical addition of
dialkylphosphonates to silicon-vinyl compounds
using benzoyl peroxide as catalyst.

$$R_3SiCH=CH_2 + HPO(OR')_2 \longrightarrow R_3SiCH_2CH_2PO(OR')_2$$
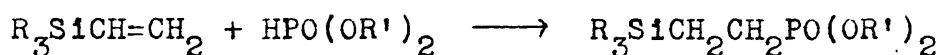
R = alkyl, alkoxyl or pentamethylsiloxanyl
R' = alkyl or aryl.

Similar reactions have been reported
with other compounds containing P-H groups.[139]
Thus, secondary phosphines, phosphine oxides and
phosphine sulphides have all undergone addition
reactions with unsaturated silanes, upon ultra-
violet irradiation:

$$e.g.\ Et_2PH + Me_2Si(CH=CH_2)_2 \xrightarrow{h\nu} (Et_2PCH_2CH_2)_2SiMe_2$$
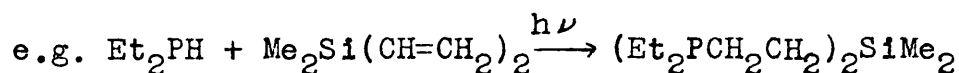
The addition of silicon hydrides to olefinic bonds attached to phosphorus, in the presence of a free radical catalyst, has been used to prepare γ-silicon-substituted derivatives of diethyl n-propylphosphonate.[140]

$$R_3SiH + CH_2:CHCH_2PO(OEt)_2$$

$$\downarrow (PhCO_2)_2$$

$$R_3SiCH_2CH_2CH_2PO(OEt)_2$$

$$R = EtO \text{ or } Et.$$
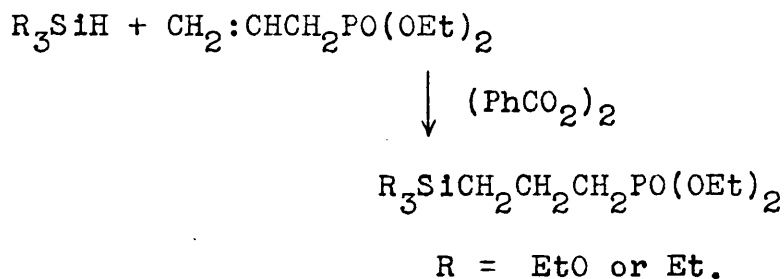
Platinic chloride may also be used to catalyse this type of addition reaction.[141] Trichlorosilane was reacted with alkylphosphonic dichloride to give trichlorosilylpropylphosphonic dichloride. Similarly prepared were dichloromethylsilylpropylphosphonic dichloride and dichloroethylsilylpropylphosphonic dichloride.

The Reactions of Organophosphorus Compounds Containing Silicon

Pyrolyses

Arbusov and Pudovic[132] found that diethyl

trimethylsilylphosphonate decomposed completely,
within 2-3 minutes, when heated to 200°, giving
tetraethoxysilane. In contrast to this, Parshall
and Lindsay[142] reported that tris(trimethylsilyl)
phosphine could be refluxed at 243°, in an inert
atmosphere, for eight hours, with very little
decomposition taking place.

A thorough investigation of the thermal
decomposition of a wide range of compounds, in
which silicon is joined to phosphorus through a
saturated carbon linkage, has been made.[23,143]
The results of this study are summarised in table VII.

It can be seen that the most stable of
these compounds is dimethyl trimethylsilylethyl-
phosphonate, which showed very little decomposition
when heated for 26 hr. at 222-284°. Dialkyl
trimethylsilylmethylphosphonates exhibited an
extremely low order of thermal stability, due, in
the case of di-n-butyl and di-n-pentyl trimethyl-
silylmethylphosphonate, to the elimination of
olefine from the ester group, leaving an acidic
function , which at the high temperatures involved,
attached the silicon-carbon bonds. In the pyrolyses

Table XV. Thermal decomposition of some organo-phosphorus compounds containing silicon

Compound	Liquid Temperature	Time (hr.)	Products (% yield)
$Me_3SiCH_2PO(OMe)_2$	225–207°	20	Me_3SiOMe,45; $MePO(OMe)_2$,30
$Me_3SiOSiMe_2CH_2PO(OMe)_2$	238–194°	10.5	Starting compound,22; $Me_3SiOSiMe_2OMe$,19; $MePO(OMe)_2$,22
$Me_3SiOSiMe_2CH_2PO(OEt)_2$	238–172°	16.5	$Me_3SiOSiMe_2OEt$,50; $MePO(OEt)_2$,37.
$Me_3SiMe_2CH_2PO(OPr^n)_2$	265–202°	16	$Me_3SiOSiMe_2OPr^n$,43; $MeCH=CH_2$
$Me_3SiCH_2PO(OPr^n)_2$	243–215°	22	Me_3SiOPr^n,31.5; $MeCH=CH_2$.
$Me_3SiCH_2PO(OBu^n)_2$	243–370°	12	$EtCH\ CH_2$,75; $(Me_3Si)_2O$,73.
$Me_3SiOSiMe_2CH_2PO(OBu^n)_2$	272–204°	7	$Me_3SiOSiMe_2.OBu^n$,62; $EtCH=CH_2$

$Me_3SiCH_2PO(OC_5H_{11})_2$	270-360°	2	n-PrCH=CH$_2$,62; (Me$_3$Si)$_2$O,16.
$PhMe_2SiCH_2PO(OBu^n)_2$	310-210°	10.5	EtCH=CH$_2$,54;C$_6$H$_6$,66.
$(p-MeC_6H_6)Me_2SiCH_2PO(OBu^n)_2$	244-360°	15.5	EtCH=CH$_2$,83;PhMe,64.
$(p-ClC_6H_4)Me_2SiCH_2PO(OBu^n)$	314-170°	10	EtCH=CH$_2$,64;PhCl,43.
$(Me_3SiCH_2)_3PO$	261-217°	22	(Me$_3$Si)$_2$O,30.
$(EtO)_3SiCH_2CH_2PO(OMe)_2$	261-240°	23	MeOH,23-36;C$_2$H$_4$,79.
$Et_3SiCH_2CH_2PO(OMe)_2$	222-284°	26	Starting compound,73; MeOH,20;Et$_3$SiOMe,14.

The yields are based on the amount of unreacted starting material.

of dimethyl trimethylsilylmethylphosphonate and

di-n-propyl trimethylsilylmethylphosphonate,

alkoxytrimethylsilanes were isolated. The following

mechanism was proposed to account for this:

$$\text{Me}_3\text{Si} \quad \text{OR}$$
$$\text{H}_2\text{C}-\!-\!-\text{P(O)OR} \longrightarrow \text{Me}_3\text{SiOR} + \text{CH}_2\!=\!\text{P(O)OR}$$

$$R = \text{Me and n-Pr}$$
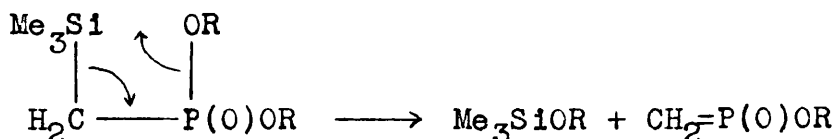
Hydrolytic reactions

Compounds containing silicon-phosphorus

linkages are readily attacked by water. Keeber

and Post[133] found that di-n-butyl trimethylsilyl-

phosphonate was decomposed by refluxing in water

for four hours, giving hexamethyldisiloxane and

phosphorous acid. The silicon-carbon bond was also

cleaved by the action of methanol or phenol:

$$\text{Me}_3\text{SiPO(OBu}^n)_2 \xrightarrow{\text{MeOH}} \text{Me}_3\text{SiOMe} + \text{HPO(OBu}^n)_2 \quad \text{(ref. 133)}$$

$$\text{Me}_3\text{SiPO(OBu}^n)_2 \xrightarrow{\text{PhOH}} \text{Me}_3\text{SiPOPh} + \text{HPO(OBu}^n)_2 \quad \text{(ref. 133)}$$
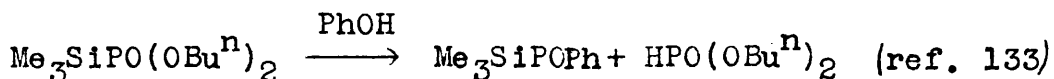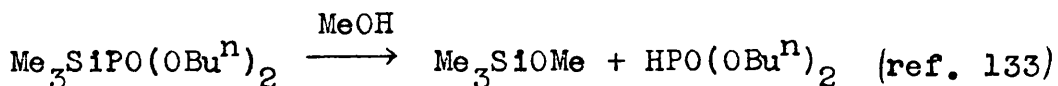
Newlands[134] has shown that dimethyl

and di-n-butyl trimethylsilylphosphonates decompose

slowly in air, but rapidly in water. However,

dibenzyl triphenylsilylphosphonate was stable to
water but was readily hydrolysed by 10% aqueous
potassium hydroxide.

The introduction of one or more carbon
atoms between the silicon and the phosphorus
atoms confirms a far greater hydrolytic stability
on the system. Keeber and Post[133] hydrolysed
di-n-butyl trimethylsilylmethylphosphonic acid by
refluxing in dilute hydrochloric acid. Refluxing
dimethyl trimethylsilylethylphosphonate with
concentrated hydrochloric acid for 24 hr. gave
triethylsilylethylphosphonic acid. However, it
is interesting to note that di-n-butyl pentamethyl-
disiloxanylmethylphosphonate is cleaved in both
acid and basic media at the phosphorus-substituted
carbon-silicon bond.

Barns and David[144] have investigated
the action of concentrated hydrochloric acid on
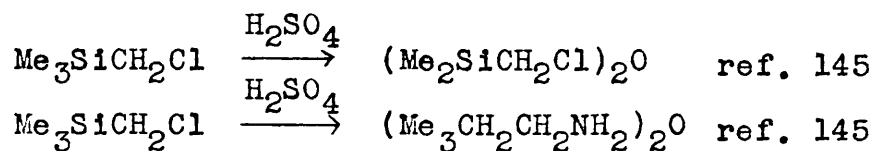a number of organophosphorus compounds containing
silicon:

$$R_3Si(CH_2)_nPO(OR')_2$$
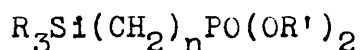
R = EtO and Me; R' = Et and n-Bu; n = 2 or 3.

In each case the $\equiv Si(CH_2)_nP\equiv$ linkage remained

intact and only the functional groups attached to

silicon and phosphorus were hydrolysed. The action

of $0.9\underline{N}$ sodium hydroxide was also studied and it

was found that both silicon- and phosphorus-carbon

bonds remained intact.

The cleavage of alkyl groups from silicon

by concentrated sulphuric acid is well-known.

Examples of this type of cleavage are given below:

$$Me_3SiCH_2Cl \xrightarrow{H_2SO_4} (Me_2SiCH_2Cl)_2O \quad ref. \ 145$$

$$Me_3SiCH_2Cl \xrightarrow{H_2SO_4} (Me_3CH_2CH_2NH_2)_2O \ ref. \ 145$$

The methyl group, in each case, is removed as

methane and only one methyl group is removed.

When tris(trimethylsilylmethyl)phosphine oxide

was treated with concentrated sulphuric acid,

at $90-100^\circ$, one methyl group was lost from each

silicon atom, giving the phosphine oxide,

$(HOSiMe_2CH_2)_3PO.$[146]
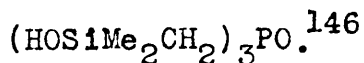
CHAPTER VI

Discussion of Experimental Results

Discussion of Experimental Results

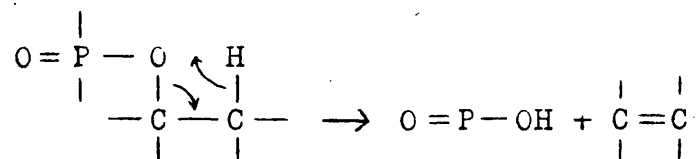1. Pyrolysis of dialkyl n-hexylphosphonates

Canavan[23] showed that di-n-butyl
ethylphosphonate, when pyrolysed, eliminated
but-1-ene giving ethylphosphonic acid in high
yield. Similarly, di-n-butyl n-hexylphosphonate
gave n-hexylphosphonic acid, together with but-1-ene.

This behaviour is paralleled by phosphates
containing alkyl groups. Thus diphenylcyclohexyl-
phosphate gave diphenylphosphate and cyclohexene.[147]
Similarly, Lecocq and Todd[148] obtained diphenylphos-
phate from the pyrolyses of diphenylisopropylphos-
phate. When dimethyl-n-hexylphosphate was passed
down a glass-helix-packed column at $300-500^\circ$,
an isomeric mixture of hex-1-ene, cis-2- and
trans-2-hexene was obtained.[149]

The pyrolyses of dialkyl n-hexylphosphonates
$n\text{-}C_6H_{13}PO(OR)_2$; R = Et, Pr^n, Pr^i, and Bu^s
indicated that the ease of the reaction and the
purity of n-hexylphosphonic acid obtained,
increased with greater chain branching in the
alkyl group. In the case of diethyl n-hexyl-

phosphonate, the production of ethylene was
inferred from the observation that the gas
emerging from the pyrolysis vessel decolourised
a solution of bromine in carbon tetrachloride.
It was not until the liquid temperature had
reached 340° that decomposition was apparent, and
only a low yield of n-hexylphosphonic acid was
obtained. Dialkyl n-hexylphosphonates with
higher alkyl groups eliminated olefines at much
lower temperatures.
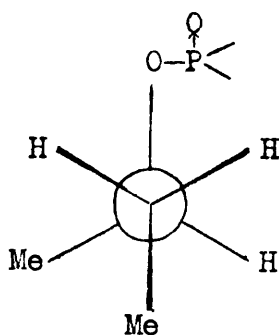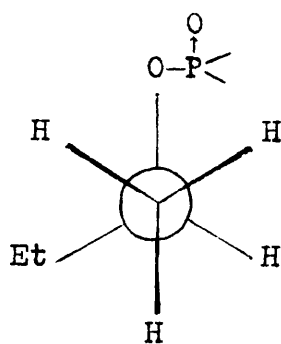
The reaction probably involves a cis-
β-elimination:

$$O=P-O \text{...} H \quad -C-C- \longrightarrow O=P-OH + C=C$$

This type of reaction is well-known for aliphatic
esters, xanthates[150] and phosphates, and has
recently been reviewed.[150]

Thus, di-methyl n-hexylphosphonate,
which has no β-hydrogen atoms, did not give
n-hexylphosphonic acid on pyrolysis, but a complex
mixture of products, among which were hex-1-ene
and dimethyl methylphosphonate, together with a

large amount of an unidentified acidic material.[143]

The pyrolysis of di-s-butyl n-hexylphosphonate gave a low-boiling material, the infrared spectrum of which indicated the presence of but-1-ene, trans-but-2-ene, and cis-but-2-ene in the approximate ratio of 6:2:1. A similar isomer distribution was observed in the thermal decomposition of s-butyl acetate.[150]

This observation again supports the view that the reaction involves a β-elimination, for in such a reaction, on purely statistical grounds, the 1-isomer would be favoured over the 2-isomer. This can be demonstrated by considering di-s-butyl n-hexylphosphonate in the following configurations:

$$\begin{array}{cc} \text{O-P}\big< & \text{O-P}\big< \\ \text{(I)} & \text{(II)} \end{array}$$

(I): O–P< at top, with H, H (upper), Et, H (lower), H (bottom)

(II): O–P< at top, with H, H (upper), Me, H (lower), Me (bottom)

(I)   (II)

Elimination from I would result in the formation of 1-butene and from II the 2-isomer would be obtained. In I there are three β-hydrogen atoms

and in II there are only two. Hence the ratio of the 1-isomer to the 2-isomer should be 3:2. The observed ratio is 2:1, but this is not considered to be a significant deviation, due to the approximate nature of the estimation. The predominance of the trans-isomer over the cis-isomer is accounted for by steric interaction between the two methyl groups in the transition state.[150]

The thermal decomposition of dialkyl alkyl- or aryl-phosphonates could be a useful route for the preparation of thermally stable phosphonic acids, which are difficult to isolate by the normal method of preparation (viz. the hydrolysis of dialkyl, alkyl or aryl-phosphonates).

2. The properties of some silicon-containing derivatives of ethylphosphonic acid

(a) Pyrolyses

In an attempt to prepare triethylsilyl-ethylphosphonic acid, di-n-butyl triethylsilyl-ethylphosphonate was pyrolysed at 250°, (the

temperature at which gas evolution began). It
was found that but-1-ene was eliminated together
with ethane. The pyrolysis residue, a glass-like
solid, was dissolved in aqueous ethanol, and
after removal of the solvent gave a viscous
liquid, which proved to be the diphosphonic acid,
$[(HO)_2OPCH_2CH_2SiEt_2]_2O$. Thus, although the
required phosphonic acid is probably formed, the
acidic groups cleaved an ethyl group from silicon.
The volume of gas evolved can be accounted for by
assuming the elimination of 2 mol. of but-1-ene
and one mol. of ethane.

To determine the minimum temperature
at which such a cleavage would occur, triethyl-
silylethylphosphonic acid was pyrolysed. Ethane
was rapidly evolved when the liquid temperature
reached 220°.

Thus, the reaction is of little value
in the preparation of trialkylsilyl-substituted
alkylphosphonic acids, since the temperature
required for the elimination reaction is
approximately the same as that at which the cleavage
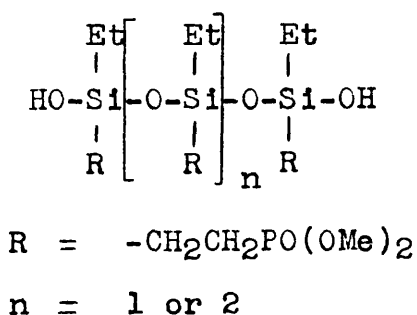reaction occurs.

(b) Solvolysis reactions

Dimethyl triethylsilylethylphosphonate was
hydrolysed by refluxing with concentrated
hydrochloric acid for seven hours. Triethyl-
silylethylphosphonic acid was isolated in high
yield and apparently no other cleavage reaction
occurred. Hydrolysis under alkaline conditions
gave the expected half-ester, methyl triethylsilyl-
ethylphosphonic acid, $Et_3SiCH_2CH_2PO(OH)(OMe)$, in
virtually quantitative yield. Again no silicon-
carbon bond cleavage could be detected.

As has been pointed out, the system
$Me_3SiOSiMe_2.CH_2PO(OR)_2$ is unstable to hydrolysis
by both acids and alkali.[136] It was thought to be
of interest to study disiloxane-containing systems
in which silicon was joined to phosphorus through
two saturated carbon atoms.

Refluxing dimethyl diethylmethoxysilyl-
ethylphosphonate in weak acid solution resulted
in the hydrolysis of the -SiOEt group only.
The infrared spectrum of the product, obtained
after one distillation, showed the presence of

-SiOH groupings. Redistillation of this compound
from a crystal of iodine (a process known to
catalyse the condensation of silanols to
disiloxanes[151]) gave a product, the infrared
spectrum of which showed a much shortened -OH
absorption. Both the infrared spectrum and the
carbon and hydrogen microanalyses figures were
consistent with its being $[(MeO)_2OPCH_2CH_2SiEt_2]_2O$
containing a small amount of the uncondensed
material.

Similarly, the treatment of dimethyl
ethylmethoxysilylethylphosphonate with dilute
acid gave a product which was only partially
condensed to the siloxane. The polysiloxane
$[EtSiCH_2CH_2PO(OMe)_2]_n$ requires, C, 34.3%;
H, 7.16%. The analyses figures obtained,
C, 32.99%; H, 7.22%, are consistent with its
being:

$$
\begin{array}{c}
\text{Et} \\
| \\
\text{HO-Si-} \\
| \\
\text{R}
\end{array}
\left[
\begin{array}{c}
\text{Et} \\
| \\
\text{O-Si-} \\
| \\
\text{R}
\end{array}
\right]_n
\begin{array}{c}
\text{Et} \\
| \\
\text{O-Si-OH} \\
| \\
\text{R}
\end{array}
$$

R   = $-CH_2CH_2PO(OMe)_2$

n   =   1 or 2

Hydrolysis of dimethyl diethylmethoxy-silylethylphosphonate, by refluxing in concentrated hydrochloric acid, gave the diphosphonic acid $\left[(HO)_2OPCH_2CH_2SiEt_2\right]_2O$ in quantitative yield. Similar treatment of dimethyl ethyldimethoxysilyl-ethylphosphonate gave the polymeric acid $\left[Et\underset{O}{\overset{|}{Si}}CH_2CH_2PO(OH)_2\right]_n$.

The results indicate that $\equiv SiCH_2CH_2PO(OR)_2$ (R = H or Me) systems are extremely stable to acid hydrolysis, even when silicon-oxygen bonds are present.

Treatment of triethylsilylethylphosphonic acid with concentrated sulphuric acid, at $100°$, led to the smooth cleavage of one ethyl group from silicon. The diphosphonic acid, $\left[(HO)_2OPCH_2CH_2SiEt_2\right]_2O$ was isolated from the reaction mixture in almost quantitative yield.

(c) Reactions with chlorinating agents
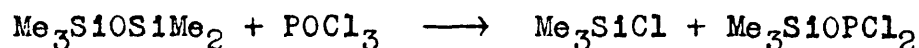
Thionyl chloride

Thionyl chloride is known to react with alkylphosphonic acids to give the corresponding

alkylphosphonic dichloride;[152,153] thus, triethyl-
silylethylphosphonic acid, when heated with an
excess of thionyl chloride, at reflux temperature,
gave triethylsilylethylphosphonic dichloride.
However, Graham and Thompson[146] report that no
trimethylsilylmethylphosphonic dichloride was
obtained when thionyl chloride was reacted with
trimethylsilylmethylphosphonic acid.

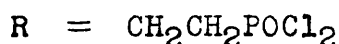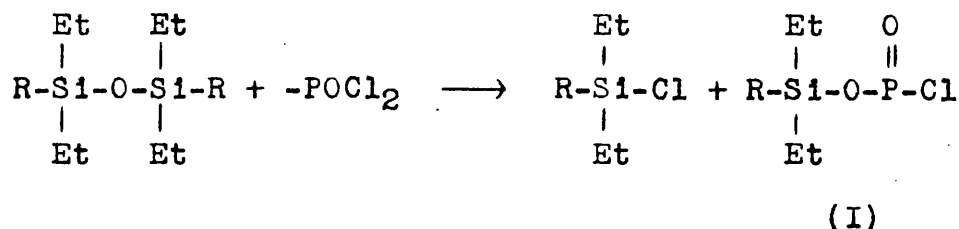In an attempt to prepare triethylsilyl-
ethylphosphonic dichloride directly from the
phosphonate, di-n-butyl triethylsilylethylphos-
phonate was refluxed with excess thionyl chloride.
It was found that only one of the alkoxy groups
was replaced, n-butyl triethylsilylethylphosphonic
chlorode being obtained.

Thionyl chloride when reacted with
$[(HO)_2OPCH_2CH_2SiMe_2]_2O$ not only chlorinated the
-OH groups but also cleaved the disiloxane linkage,
giving chlorodiethylsilylethylphosphonic dichloride.
Disiloxane linkages are not normally cleaved by
thionyl chloride alone, but require the presence
of aluminium chloride[154] or hydrogen chloride.[155]
P-Cl groups may catalyse the cleavage reaction

in this case in a similar way. However, it is
known that phosphorus oxychloride will cleave
hexamethyldisiloxane, giving trimethylsilyl-
phosphorochloridate.[155]

$$Me_3SiOSiMe_2 + POCl_3 \longrightarrow Me_3SiCl + Me_3SiOPCl_2$$

Thus, it is possible that the phosphorus halide
attacks the disiloxane linkage according to the
following reaction scheme:

$$
\begin{array}{c}
\overset{\displaystyle Et}{\underset{\displaystyle Et}{\overset{|}{\underset{|}{R-Si}}}}-O-\overset{\displaystyle Et}{\underset{\displaystyle Et}{\overset{|}{\underset{|}{Si}}}}-R + -POCl_2 \longrightarrow \overset{\displaystyle Et}{\underset{\displaystyle Et}{\overset{|}{\underset{|}{R-Si}}}}-Cl + \overset{\displaystyle Et}{\underset{\displaystyle Et}{\overset{|}{\underset{|}{R-Si}}}}-O-\overset{\displaystyle O}{\overset{\|}{P}}-Cl
\end{array}
$$

(I)

$$R = CH_2CH_2POCl_2$$

Thionyl chloride could then possibly attack the
-Si-O-P- linkage, giving chlorodiethylsilylethyl-
phosphonic dichloride.

Phosphorus pentachloride

Alkylphosphonic dichlorides may be
prepared from dialkyl alkylphosphonates by
treatment with phosphorus pentachloride;[156]
dimethyl triethylsilylethylphosphonate when

reacted in this way gave triethylsilylethylphosphonic
dichloride in high yield.

(d) Reactions with organometallic reagents

Dimethyl triethylsilylethylphosphonate,
when refluxed with methylmagnesium iodide in ether,
gave a crystalline complex containing iodine. The
compound could not be identified but it appears
that complexing occurred via the phosphoryl bond,
with the magnesium salt formed in the replacement
reaction. The infrared spectrum of the compound
indicated the absence of P-O-Me groupings. Organo-
phosphine oxides are known to form complexes with
metallic halides.[157]

Phenyl-lithium was refluxed with dimethyl
triethylsilylethylphosphonate in ether, for four
hours, and gave diphenyltriethylsilylethylphosphine
oxide in high yield. Ethyl-lithium, when added to
dimethyl triethylsilylethylphosphonate at 0° (ethyl-
lithium reacts with ether rapidly at temperatures
above 0°) gave unidentified products the
infrared spectrum of which indicated the presence
of -P-O-Me groupings.[158] It appears that more severe

conditions are required for lithium-alkyls to replace methoxy groups attached to phosphorus.

Diethyltriethylsilylethylphosphine oxide was successfully prepared by the reaction of ethyllithium with triethylsilylethylphosphonic dichloride.

EXPERIMENTAL SECTION

EXPERIMENTAL

1. General Techniques.

The general experimental techniques have been described in Part I.

Free radical addition reactions were carried out in three-necked flasks fitted with a stirrer, reflux condenser and a dropping funnel. The free radical initiator, benzoyl peroxide, (recrystallised from chloroform) was added to the reaction mixture, in small portions, down the reflux condenser.

Infrared spectra.- The infrared spectra of gases evolved in pyrolyses and cleavage reactions were determined on the Perkin-Elmer "Infracord". The gas was collected in a gas burette and a portion of this was passed into a 10 cm. cell, which had previously been flushed with dry nitrogen. Alternatively, the gas was trapped in a Drikold/alcohol trap and distilled from this into the gas cell. The concentration of the gas in the cell was adjusted by adding small volumes of nitrogen.

The spectra of liquids were taken as thin

films, and of solids as Nujol mulls, between rock salt plates.

pH Titrations.- Neutral equivalents (N.E.) of acidic products were determined on a W.G. Pye and Co. Ltd., pH meter, Catalogue No. 11068, using a glass and a potassium chloride electrode.

A solution of the acid in aqueous ethanol (50 vol.%) was titrated against 0.1N sodium hydroxide solution. So that the titration curve could also be used to give an estimate of the pK_a of the acid an equal volume of ethanol was added after each addition of sodium hydroxide solution.

2. The preparation and pyrolysis of some dialkyl n-hexylphosphonates.

Preparations.

Diethyl n-hexylphosphonate.- This was prepared by the modified Arbusov reaction as used by Kosolopoff.[158]

Diethylphosphonate (39.55 g., 0.25 mole) was added slowly to sodium (5.75 g., 0.25 g.-atom) in 60-80° light petroleum (200 ml.) and the mixture refluxed until solution of the sodium was complete.

n-Hexyl bromide (41.25 g., 0.25 mole) was then added
slowly and after addition the mixture was refluxed
for 6 hr. Sodium bromide was filtered off and the
solution washed with water, dried over anhydrous
sodium sulphate and the solvent removed. Fraction-
ation of the oil gave 38.8 g., (73%) of diethyl
n-hexylphosphonate, b.p. 98°/1.5 mm., n_D^{25} 1.4300,
(lit.[159] 103°/2 mm., n_D^{17} 1.4311).

Similarly prepared were:

Di-n-propyl n-hexylphosphonate.- 53% yield, b.p.
109-110°/0.45 mm., n_D^{20} 1.4360 (Found: C, 57.53;
H, 11.22. $C_{12}H_{27}O_3P$ requires C, 57.60; H, 10.8%).

Di-isopropyl n-hexylphosphonate.- 48% yield, b.p.
111.5-113°/0.45 mm., n_D^{25} 1.4360 (Found: C, 57.53;
H, 11.22%).

Di-n-butyl n-hexylphosphonate.- 34% yield, b.p.
125-128°/1.0 mm., n_D^{20} 1.5335 (Found: C, 60.99,
H, 10.99%).

The pyrolysis of dialkyl n-hexylphosphonates.

General.

Pyrolyses were carried out in round-

bottomed pyrex flasks fitted with a reflux condenser, thermometer (to measure the liquid temperature) and a nitrogen inlet tube. Volatile products were led from the top of the reflux condenser to cold-trap immersed in a Drikold/alcohol slurry. In most cases the weight of the flask and contents was taken before and after pyrolyses. In the case of diethyl n-hexyl-phosphonate, gas emerging from the cold-trap was bubbled through a solution of bromide in carbon tetrachloride. Heating was effected using a small heating mantle connected to a Variac, variable transformer.

Diethyl n-hexylphosphonate.-

Diethyl n-hexylphosphonate (10 g.) was placed in the pyrolysis vessel and heated to 360 for 6 hr. A viscous liquid remained in the flask; this crystallised on exposure to air. During the course of the pyrolysis the bromine/carbon tetrachloride solution was decolourized. The solid (m.p. 57-58°) was recrystallised from 60-80 light petroleum to give n-hexylphosphonic acid, m.p. 104-105° (lit.,[158] n-hexylphosphonic acid, m.p. 104.5-106°). The liquid in the cold-trap (1.2 g.) smelled of phosphines. No attempt was made to identify this.

Di-n-propyl n-hexylphosphonate.-

Di-n-propyl n-hexylphosphonate (10 g.)
when heated similarly gave vigorous gas evolution
at 236^c. After 2.5 hr., when gas evolution had
ceased, the temperature had reached 360^c. The flask
was cooled and a white, crystalline solid, m.p.
45-50°, remained. The loss in weight (3.15 g.)
corresponded to the evolution of 94% of the theor-
etical amount of propene, which was identified by
its infrared spectrum. Recrystallization of the
residue gave n-hexylphosphonic acid (75% yield),
m.p. 104-105°.

Di-isopropyl n-hexylphosphonate.-

Di-isopropyl n-hexylphosphonate (8.05 g.)
was pyrolysed as above. Gas was evolved when the
temperature reached 210-220° (after 10 min.) and
became vigorous at 260° (after 15 min.). The
temperature then fell rapidly to 220°, and after
25 min. gas evolution had stopped and the temper-
ature had reached 275°. The loss in weight corresp-
onded to a quantitive evolution of propene which
was identified by its infrared spectrum. The
residue, a white solid, was recrystallised to give

n-hexylphosphonic acid, m.p. 104-105°, in 83% yield.

Di-s-butyl n-hexylphosphonic acid.-

Di-s-butyl n-hexylphosphonic acid (9.4 g.) was pyrolysed as before. In 5 min. the temperature had reached 240° and gas evolution was observed: this became vigorous after 8 min., when the temperature had reached 255°. The temperature then fell rapidly to 210° and after 14 min., when the temperature had risen to 220°, gas evolution had ceased. The loss in weight corresponded to the quantitative evolution of butene, which was collected in 85% yield, and shown by its infrared spectrum to be a mixture of but-1-ene and cis- and trans-but-2-enes, in the ratio 6:1:2. The residue (m.p. 86-88°) was recystallized once to give n-hexylphosphonic acid, m.p.104.5°, in 90% yield.

3. The preparation of organosilicon-containing derivatives of ethylphosphonic acid

(a) Preparation of organosilicon compounds.

Triethylvinylsilane.- To the Grignard reagent from ethylbromide (4.0 mole) and magnesium

(4.0 g.-atom) was added trichlorovinylsilane

(1.0 mole). After addition the mixture was

refluxed for 14 hr. Working up in the usual way

gave, on fractionation, 96.5 g. (75%) of triethyl-

vinylsilane, b.p. 145-148°, n_D^{20} 1.4342 (lit.[160]

146°, n_D^{20} 1.4330).

Trimethoxyvinylsilane.-

(i) An attempt was made to prepare this compound

by the method of Nagel, Tamborski and Post.[161]

    Trichlorovinylsilane (1.0 mole) was added

to methyl alcohol (4 mole) and the mixture refluxed

for 9 hr. Fractionation gave a large volume of

liquid, b.p. 67.5-78.5°; 21.5 g. of trimethoxy-

vinylsilane, b.p. 51.5-52°/48-49 mm., (lit.[161]

55.9°/62 mm.) and 22.5 g. of sym-tetramethyldivinyl-

disiloxane, b.p. 118°/48 mm., n_D^{20} 1.4128 (lit.[161]

120-120.6°/46 mm., n_D^{25} 1.4172).

(ii) Sodium methoxide (3 mole) was prepared by the

addition of sodium (70.5 g., 3.0 g.-atom) to

anhydrous methanol (400 ml.). Excess methanol

was distilled off and the resulting dry sodium

methoxide broken up under anhydrous ether (300 ml.).

Trichlorovinylsilane (1.0 mole) was added slowly
and the mixture refluxed and stirred for 2 hr.
The precipitated sodium chloride was filtered off
and washed with 60-80° light petroleum. Fraction-
ation, after removal of the combined solvents,
gave 109.3 g. (75.5%) of trimethoxyvinylsilane,
b.p. 51-52°/48-50 mm., n_D^{20} 1.3948.

Diethyl methoxyvinylsilane.- The Grignard reagent
from ethyl bromide (121.1 g., 1.1 mole) and
magnesium (26.5 g., 1.1 g.-atom) was filtered and
added to trimethoxyvinylsilane (72.5 g., 0.5 mole)
in ether (250 ml.). After the addition the mixture
was refluxed for 1 hr., filtered and fractionated
to give 39.5 g. (55%) of diethylmethoxyvinylsilane,
b.p. 136-136.5°, n_D^{20} 1.4202, d_{20} 0.8311. (Found:
M.R., 43.9; C, 58.25; H, 11.18. $C_6H_{16}OSi$ requires
M.R., 44.1; C, 58.4; H, 11.12%).

Dimethoxyethylvinylsilane.- This compound was
prepared as above using equi-molecular quantities
of ethylmagnesium bromide and trimethoxyvinylsilane.
Fractionation gave dimethoxyethylvinylsilane,
(49%) b.p. 130.5°, n_D^{25} 1.3991, d_{25} 0.8987.
(Found: M.R., 39.5; C, 47.73; H, 9.62. $C_6H_{14}O_2Si$

requires M.R., 40.3; C, 47.2; H, 9.59%).

(b) The preparation of organosilicon-containing
derivatives of dialkyl ethylphosphonates.

Dimethyl triethylsilylethylphosphonate.- Dimethyl
phosphonate (66.0 g., 0.6 mole) and triethylvinyl-
silane (71.15 g., 0.5 mole) were refluxed for 14 hr.,
during which time benzoyl peroxide (4.0 g.) was
added in 0.2 g. lots. Fractionation gave 51.0 g.
(45.6%) of dimethyl triethylsilylethylphosphonate,
b.p. 153-154°/10 mm., n_D^{20} 1.4532 (lit.[23] b.p.
150-153°/10 mm., n_D^{20} 1.4527).

Similarly prepared were:

Di-n-butyl triethylsilylethylphosphonate.- 34%
yield, b.p. 175-176°/1.5 mm., n_D^{20} 1.4514 (Found:
C, 57.25; H, 10.93. $C_{16}H_{37}O_3PSi$ requires C, 57.15;
H, 11.01%).

Di-isopropyl triethylsilylethylphosphonate.- 34%
yield, b.p. 135-136°/1.5 mm., n_D^{20} 1.4458 (Found:
C, 54.7; H, 11.44. $C_{14}H_{33}O_3PSi$ requires C, 57.4;
H, 11.41%).

Dimethyl diethylmethoxysilylethylphosphonate.- 64%
yield, b.p. 130-134°/3-4 mm., n_D^{20} 1.4458 (Found:

C, 42.65; H, 9.25. $C_9H_{23}O_4PSi$ requires C, 42.5;
H, 9.06%).

Dimethyl dimethoxyethylsilylethylphosphonate.-
36% yield, b.p. 130-132°/1.2 mm., n_D^{25} 1.4338
(Found: C, 37.58; H, 8.09. $C_8H_{21}O_5PSi$ requires
C, 37.60; H, 7.9%).

4. The reactions of some organosilicon-containing
derivatives of ethylphosphonic acid

(a) Pyrolyses.
Di-n-butyl triethylsilylethylphosphonate.-
(1) Di-n-butyl triethylsilylethylphosphonate (15 g.,
0.0447 mole) was heated to 300°, when vigorous
gas evolution took place. After 30 mm. the
temperature had fallen to 278° and gas evolution
had ceased. The residue (a glass) became sticky
on exposure to the atmosphere and when dissolved
in aqueous ethanol gave an acidic solution.
Removal of the solvent gave a sticky, viscous
oil. A pH titration of this compound in aqueous
ethanol (50 vol.%) gave a curve corresponding to
that of a dibasic acid, 1st N.E. 201 (pK_{a_1} 3.9);
2nd N.E. 100.2 (pK_{a_2} 9.38). The volatile material
in the cold-trap was distilled into a 10 cm.
infrared gas cell. The infrared spectrum

corresponded to that of but-1-ene.

(ii) Di-n-butyl triethylsilylethylphosphonate

(1.2893 g.) was pyrolysed as before. The apparatus

was made gas tight and connected to a gas-burette.

The volume of gas evolved was 244.5 ml. and its

infrared spectrum corresponded to that of a mixture

of ethane and but-1-ene. (The elimination of 1

equivalent of ethane and 2 equivalents of but-1-ene

would have given 256.5 ml. of gas.

Triethylsilylethylphosphonic acid.

Triethylsilylethylphosphonic acid

(0.7390 g.) was heated to 280^c until gas evolution

had ceased. The volume of gas collected was 75.5

ml. and its infrared spectrum corresponded to

that of ethane. The glassy residue in the flask

was dissolved in aqueous ethanol and the solvent

removed. A pH titration of the residue gave

1st N.E. 198.5 (pK$_{a_1}$ 4.2);2nd N.E. 101.3 (pK$_{a_1}$

10.2).

(b) The action of concentrated sulphuric acid

on triethylsilylethylphosphonic acid.

Triethylsilylethylphosphonic acid

(3.63 g.) and concentrated sulphuric acid were

mixed in a 25 ml. flask and heated to 100^{c}. The

gas evolved was collected in a gas-burette: its

infrared spectrum corresponded to that of ethane,

and the volume evolved was 363.5 ml. (the

theoretical volume for the cleavage of one ethyl

group would be 364.0 ml.).

The residue in the flask was dissolved

in ether, filtered and the ether removed. Titration

in aqueous ethanol (50 vol.%) against sodium h

hydroxide (0.1N) over a pH range 3-14, indicated

a dibasic acid, 1st N.E. 188.5; 2nd N.E. 111.5.

The diphosphonic acid $[(HO)_2OPCH_2CH_2SiEt_2]_2O$

requires 1st N.E. 203; 2nd N.E. 101.5.

(c) <u>Hydrolysis</u> <u>of</u> <u>dimethyl</u> <u>triethylsilylethylphos-</u>
<u>phonate</u>.

(i) <u>Concentrated</u> <u>hydrochloric</u> <u>acid</u>.- Dimethyl

triethylsilylethylphosphonate (25.2 g., 0.1 mole)

was refluxed with concentrated hydrochloric acid

(150 ml.) for 7 hr. to give a white solid, which

was filtered off, washed with water and dried

on a filter-pad. Recrystallisation from $60-80^{c}$.

light petroleum gave 15.7 g. (75%) of triethyl-
silylethylphosphonic acid, m.p. 112-114° (lit.[23]
114°).

(ii) <u>Dilute potassium hydroxide</u>.- Dimethyl
triethylsilylethylphosphonate (4.3 g.) was
refluxed with 1$\underline{N}$ potassium hydroxide solution
(25 ml.) until the mixture became homogeneous.
The solution was acidified, extracted with ether
and the ether removed to give a colourless oil
(n_D^{25} 1.4563). A pH titration against 0.1$\underline{N}$ sodium
hydroxide, in aqueous ethanol, (50 vol.%) gave a
curve corresponding to that for a mono-basic acid.
(Found: N.E. 240 (pK_a 3.30). The mono-ester
$Et_3SiCH_2CH_2PO(OH)(OMe)$ requires N.E. 238 .

(d) <u>Hydrolysis of dimethyl diethylmethoxysilyl-
ethylphosphonate</u>.

(i) <u>Dilute hydrochloric acid</u>.- Dimethyl diethyl-
methoxysilylethylphosphonate (15 g.) was mixed
with water (30 ml.) dioxan (70 ml.) and
concentrated hydrochloric acid (0.5 ml.) and the
mixture was refluxed for 30 min. before being
poured into water and extracted with ether.

Removal of thé solvent gave a colourless oil (n_D^{20} 1.4628) which was dried at 60^c and 10 mm. for 1 hr. The infrared spectrum indicated the presence of -OH groupings and even after further drying the -OH band persisted. Redistillation, after the addition of a crystal of iodine, gave a colourless liquid, b.p. $178°/0.05$ mm., n_D^{25} 1.4589. The infrared spectrum showed a much reduced -OH band and was consistant with its being the compound $[(MeO)_2(O)PCH_2CH_2SiEt_2]_2O$ (Found: C, 42.25; H, 9.93. $C_{16}H_{40}O_7P_2Si_2$ requires C, 41.6; H, 8. 66%).

(ii) Concentrated hydrochloric acid.- Dimethyl diethylmethoxysilylethylphosphonate (16 g.) was refluxed with concentrated hydrochloric acid for 12 hr. The viscous oil which separated was removed and stripped of volatiles. The oil would not crystallise and was acid to litmus in aqueous ethanol. A pH titration gave 1st N.E. 200.5; 2nd N.E. 101.3. (The acid $[(HO)_2OPCH_2CH_2SiEt_2]_2O$, requires 1st N.E. 203.0; 2nd N.E. 101.5).

(e) Hydrolysis of dimethyl dimethoxyethylsilyl-ethylphosphonate

(i) <u>Dilute hydrochloric acid</u>.- Dimethyl dimethoxy-
ethylsilylethylphosphonate (15 g.) was hydrolysed
as above. The solution was poured into water
and extracted with ether. Removal of the solvent
left a colourless oil which was dried at 0.1 mm.
and room temperature for 3 hr. The infrared
spectrum indicated the presence of -OH groupings.
Further drying at 0.1 mm. and 78° for 12 hr. did
not reduce the -OH absorption (Found: C, 32.99;
H, 7.22%).

(ii) <u>Concentrated hydrochloric acid</u>.- Dimethyl
dimethoxyethylsilylethylphosphonate (6.5 g.)
was refluxed with concentrated hydrochloric acid
(20 ml.) for 5 hr. The product would not
precipitate on dilution and so all volatiles
were removed on a water bath at 15 mm., to give
a thick yellow oil. This was dissolved in
ethanol, and the solution was refluxed with
active charcoal, filtered, and the ethanol
removed to give a white, polymeric, acidic
substance (Found: N.E. 188).

(f) <u>The action of thionyl chloride on silicon-
containing derivatives of ethylphosphonic acid</u>

(i) <u>Triethylsilylethylphosphonic acid</u>.- Triethyl-
silylethylphosphonic acid (7.0 g., 0.033 mole)
was refluxed with thionyl chloride (25.0 g.) for
5 hr. Distillation, after removal of excess
thionyl chloride, gave 4.3 g. (51%) of triethyl-
silylethylphosphonic acid dichloride, b.p. 123-
124°/1.5 mm., (Found: C, 27.0. $C_8H_{19}Cl_2OPSi$
requires C, 27.2%). (lit.,[138] b.p. 140-145°/8 mm.).

(ii) <u>Di-n-butyl triethylsilylethylphosphonate</u>.-
Di-n-butyl triethylsilylethylphosphonate (15.0 g.,
0.044 mole) was refluxed with thionyl chloride
(30 g.) for 5 hr. Distillation gave 8 g. of a
liquid, b.p. 135°/2.5 mm., n_D^{25} 1.4635, the infra-
red spectrum of which indicated the presence of
-P-O-Bu^n groupings (Found: Cl, 11.6%).

(iii) $[(HO)_2(O)PCH_2CH_2SiEt_2]_2O$.- The acid (6.0 g.)
was refluxed with thionyl chloride (25 g.) for
5 hr. Distillation of the residue, after removal
of excess thionyl chloride at the pump, gave
4.3 g. of diethylchlorosilylethylphosphonic acid
dichloride, b.p. 98-102°/0.5-0.6 mm., n_D^{25} 1.4902
(lit.[138] b.p. 143-148°/8.8 mm., n_D^{25} 1.4918)
(Found: Cl. 37.6. $C_6H_{14}Cl_3POSi$ requires Cl,

39.7%).

(g) <u>The reaction of phosphorus pentachloride with
dimethyl triethylsilylethylphosphonate.</u>- Dimethyl
triethylsilylethylphosphonate (25.2 g., 0.1 mole)
was mixed with phosphorus pentachloride (41.6 g.,
0.2 mole). The reaction was vigorous at first
and after the rapid boiling had subsided the
mixture was heated to not more than 150°.
Phosphorus oxychloride was continuously removed
and a total of 30.5 g. (95% of the theoretical
amount) collected. The residue was distilled
to give 12.5 g. (50%) of triethylsilylethyl-
phosphonic acid dichloride, b.p. 123°/1.5 mm.,
n_D^{25} 1.4880. (lit.[138] b.p. 140-146°/8 mm., n_D^{20}
1.4895).

(h) <u>The attempted preparation of dimethyl
triethylsilylethylphosphine oxide</u>

(i) Di-methyl triethylsilylethylphosphonate
(40 g., 0.159 mole) was added slowly to the
Grignard reagent from methyl iodide (0.4 mole)
and magnesium (0.4 g.-atom) and refluxed for
78 hr., when two layers were observed in the

reaction vessel. Working up in the usual way,
and removal of the ether gave a brown oil, small
portions of which were crystallised slowly from
benzene, on clock glasses. Recrystallisation
from 60-80° light petroleum gave white needles,
m.p. 118°. (Found: C, 42.55; H, 9.55%). The
infrared spectrum of the complex showed the
absence of P-O-Me groupings. On treatment with
concentrated sulphuric acid, iodine was liberated
(Found: I, 22.5%).

(ii) A similar complex was obtained by the reaction
of methylmagnesium chloride with dimethyl triethyl-
silylethylphosphonate.

(i) The action of organolithium reagents on
dimethyl triethylsilylethylphosphonate and its
derivatives.

(1) Dimethyl triethylsilylethylphosphonate(12.5 g.,
0.05 mole) was added to phenyl-lithium (0.13 mole)
in ether. The mixture was refluxed for 4 hr.
and worked up in the usual way to give a viscous
oil, distillation of which gave diphenyl, b.p.
125-130°/1.0 mm. (which condensed as a white

solid in the condenser) and a residue which
sublimed at $140^{\circ}/1.0$ mm. The sublimate (m.p. $78-85^{\circ}$)
was recrystallised from $60-80^{\circ}$ light petroleum to
give diphenyltrimethylsilylethylphosphine oxide,
m.p. $103-104^{\circ}$ (Found: C, 69.75; H, 8.75. $C_{20}H_{31}OPSi$
requires C, 69.75; H, 8.44%).

(ii) Dimethyl triethylsilylethylphosphonate (12.5 g.,
0.05 mole) was added to ethyl-lithium (0.13 mole)
in ether at 0°. When all the phosphonate had been
added the mixture was allowed to warm to room
temperature and was worked up in the usual way.
Distillation gave unidentified products, the
infrared spectra of which indicated the presence
of P-O-Me groupings.

(iii) Triethylsilylethylphosphonic acid dichloride
(12.5 g.,0.05 mole) was added to ethyl-lithium
(0.26 mole), the mixture being kept below 0°.
Working up in the usual way and fractionation on
a 12 inch Vigreux column gave 4.2 g. (34%) of
diethyltriethylsilylethylphosphine oxide, b.p.
$136-137^{\circ}/0.8$ mm., n_D^{20} 1.4738 (Found: C, 58.25;
H, 11.70. $C_{12}H_{29}OPSi$ requires C, 58.10; H, 11.68%).

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