112. *Organosilicon Compounds. Part XXII.*[1] *The Thermal Decomposition of Some Silicon-substituted Organophosphorus Compounds.*

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We have studied the decomposition of some compounds containing silicon linked to phosphorus through carbon or carbon and oxygen when refluxed in a nitrogen atmosphere. They comprise phosphonates [$Me_3Si{\cdot}CH_2{\cdot}PO(OAlk)_2$, $Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}CH_2{\cdot}PO(OAlk)_2$, $ArMe_2Si{\cdot}CH_2{\cdot}PO(OBu^n)_2$, $Et_3Si{\cdot}CH_2{\cdot}CH_2PO(OMe)_2$, and $(EtO)_3Si{\cdot}CH_2{\cdot}CH_2{\cdot}PO(OMe)_2$], phosphates [$(Me_3Si{\cdot}CH_2{\cdot}O)_3PO$ and (p-$Me_3Si{\cdot}C_6H_4{\cdot}O)_3PO$], and phosphine oxides [$(Me_3Si{\cdot}CH_2)_3PO$ and $(PhMe_2Si{\cdot}CH_2)_3PO$]. The silicon-containing compounds are on the whole not markedly less stable than comparable simple organophosphorus compounds; a feature is the tendency for the organosilicon groups to come away with oxygen originally attached to phosphorus. Dimethyl 2-triethylsilylethylphosphonate and tris(trimethylsilylmethyl)phosphine oxide show considerable thermal stability.

It is possible that useful modifications might be made to silicones by the introduction of organophosphorus side-groups. To provide information on the thermal stability of such materials we made a range of simple compounds having silicon attached to phosphorus through carbon or through carbon and oxygen, and examined their behaviour on being heated in glass under nitrogen.

The compounds were boiled in a stream of nitrogen in a glass flask fitted with a reflux condenser the outlet from which led to a trap cooled in solid carbon dioxide. The main results are summarized in Table 1 (only identified products are listed, details being given in the Experimental section), and the main features, with some comments, are as follows:

Table 1.

Thermal decomposition of phosphorus-containing organosilicon compounds.

Compound	Temp. of liquid	Time (hr.)	Products and yields (%) [a]
$Me_3Si{\cdot}CH_2{\cdot}PO(OMe)_2$	225—207°	20	$Me_3Si{\cdot}OMe$, 45; $Me{\cdot}PO(OMe)_2$, 30
$Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}CH_2{\cdot}PO(OMe)_2$	238—194	10·5	Starting compd. 22; $Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}OMe$, 19; $Me{\cdot}PO(OMe)_2$, 22
$Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}CH_2{\cdot}PO(OEt)_2$	238—172	16·5	$Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}OEt$, 50; $Me{\cdot}PO(OEt)_2$, 37
$Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}CH_2{\cdot}PO(OPr^n)_2$	265—202	16	$Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}OPr^n$, 43; $Me{\cdot}CH{:}CH_2$
$Me_3Si{\cdot}CH_2{\cdot}PO(OPr^n)_2$	243—215	22	$Me_3Si{\cdot}OPr^n$, 31·5; $Me{\cdot}CH{:}CH_2$
$Me_3Si{\cdot}CH_2{\cdot}PO(OBu^n)_2$	243—370	12	$Et{\cdot}CH{:}CH_2$, 75; $(Me_3Si)_2O$, 73
$Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}CH_2{\cdot}PO(OBu^n)_2$	272—204	7	$Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}OBu^n$, 62; $Et{\cdot}CH{:}CH_2$
$Me_3Si{\cdot}CH_2{\cdot}PO(OC_5H_{11})_2$	270—360	2	$Pr^n{\cdot}CH{:}CH_2$, 62; $(Me_3Si)_2O$, 16
$PhMe_2Si{\cdot}CH_2{\cdot}PO(OBu^n)_2$	310—210	10·5	$Et{\cdot}CH{:}CH_2$, 54; C_6H_6, 66
(p-$Me{\cdot}C_6H_4)Me_2Si{\cdot}CH_2{\cdot}PO(OBu^n)_2$	244—360	15·5	$Et{\cdot}CH{:}CH_2$, 83; PhMe, 64
(p-$Cl{\cdot}C_6H_4)Me_2Si{\cdot}CH_2{\cdot}PO(OBu^n)_2$	314—170	10	$Et{\cdot}CH{:}CH_2$, 64; PhCl, 43
$(Me_3Si{\cdot}CH_2)_3PO$	261—217	22	$(Me_3Si)_2O$, 30
$(Me_3Si{\cdot}CH_2{\cdot}O)_3PO$	268—295	38	Starting compd., 42·5
(p-$Me_3Si{\cdot}C_6H_4{\cdot}O)_3PO$	410—310	42	$(Me_3Si)_2O$, 9
$(EtO)_3Si{\cdot}CH_2{\cdot}CH_2{\cdot}PO(OMe)_2$	261—240	23	MeOH, 23—36; C_2H_4, >9%
$Et_3Si{\cdot}CH_2{\cdot}CH_2{\cdot}PO(OMe)_2$	222—284	26	Starting compd., 73; MeOH, 20; Et_3SiOMe, 14

[a] For an important comment on the method of calculating the yields see the Experimental section.

(*a*) The phosphonates $Me_3Si{\cdot}CH_2{\cdot}PO(OR)_2$, where $R = Bu^n$ or n-C_5H_{11}, break down to give but-1-ene and pent-1-ene, respectively, along with hexamethyldisiloxane. It is known that some dialkyl alkylphosphonates, $R{\cdot}PO(OR')_2$, decompose when heated to give olefin and the corresponding phosphonic acid, $R{\cdot}PO(OH)_2$;[2] the two organosilicon

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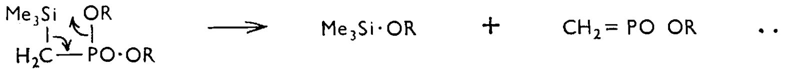
[1] Part XXI, Canavan and Eaborn, *J.*, 1959, 3751.

[2] Canavan, Dowden, and Eaborn, *J.*, 1962, 331.

phosphonates probably also initially give olefin and trimethylsilylmethylphosphonic acid, which then decomposes to give hexamethyldisiloxane. The secondary decomposition probably involves water eliminated from the phosphonic acid in the formation of anhydrides, this water, in presence of acids, either cleaving the $Me_3Si{-}CH_2$ bond directly or hydrolysing $Me_3Si{\cdot}O{\cdot}P$ links produced by attack of a phosphorus acid on this bond. [It is known that $\equiv Si{-}CH_2{\cdot}O{\cdot}PO(OR)_2$ bonds are readily cleaved by hydroxylic species,[3] even by water or alcohols under mild conditions.] The small production of hexamethyldisiloxane from the di-n-pentyl compared with that from the di-n-butyl ester, although the yields of olefin were similar, accords with this suggestion, since the former compound was heated for a much shorter time and secondary decompositions would be less extensive.

(*b*) The phosphonates $Me_3Si{\cdot}CH_2{\cdot}PO(OR)_2$, where R = Me and Pr^n, behave differently from the n-butyl and n-pentyl esters, giving the alkoxysilicon compounds $Me_3Si{\cdot}OR$ and the phosphonates $Me{\cdot}PO(OR)_2$, and little or no olefin. (Much unidentified material was also obtained, as noted in the Experimental section.) It is attractive to attribute the formation of the $Me_3Si{\cdot}OR$ compounds to a *cis*-elimination process (1), of the type which occurs readily in organosilicon compounds having an electronegative element in the β-position with respect to silicon.[4] Among other reactions of the unstable intermediate $CH_2{=}PO{\cdot}OR$ there might be addition of the alcohol ROH to give the ester $Me{\cdot}PO(OR)_2$.



. . . (1)

(Alcohol is known to be formed in thermal decomposition of a dialkyl alkylphosphonate in which olefin cannot be produced directly from the alkoxy-group, *e.g.*, of dimethyl n-hexylphosphonate,[2] and might well be formed in those decompositions of the organosilicon compounds which occur without olefin formation.) It is true that if an alcohol is formed it could give the observed products by reaction (2), but it is more satisfactory to involve the trimethylsilyl group in the first step of the breakdown, since its presence induces a mode of decomposition which takes place more readily than the olefin formation which is the main type of decomposition in the case of diethyl and di-n-propyl alkylphosphonates.

$$Me_3Si{\cdot}CH_2{\cdot}PO(OR)_2 + ROH \longrightarrow Me_3Si{\cdot}OR + Me{\cdot}PO(OR)_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

That the $Me_3Si{\cdot}CH_2{\cdot}PO(OR)_2$ compounds break down differently when R = Me from Pr^n when R = Bu^n or n-C_5H_{11}, can be attributed to greater ease of olefin formation from the larger alkyl groups.[2]

(*c*) The siloxanes $Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}CH_2{\cdot}PO(OR)_2$, where R = Me, Et, Pr^n, or Bu^n, undergo decomposition similar to that discussed under (*b*), to give $Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}OR$ and $Me{\cdot}PO(OR)_2$ compounds. (The decompositions appear to provide the first preparations of compounds of the $Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}OR$ type, but more direct preparations should be possible.) This decomposition appears to be easier with the siloxanes than with the $Me_3Si{\cdot}CH_2{\cdot}PO(OR)_2$ compounds, and thus the di-n-butyl ester, $Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}PO(OBu^n)_2$, breaks down in this way rather than giving but-1-ene, which is formed from the corresponding compound $Me_3Si{\cdot}CH_2{\cdot}PO(OBu^n)_2$.

(*d*) The compounds $ArMe_2Si{\cdot}CH_2{\cdot}PO(OBu^n)_2$ give but-1-ene and the aromatic compound, ArH. Presumably elimination of butene occurs first, and the acids produced then cleave the Ar–Si bond.

(*e*) The phosphine oxide $(Me_3Si{\cdot}CH_2)_3PO$ decomposes to give hexamethyldisiloxane, along with a range of unidentified products. The residue left in the flask was alkaline, presumably because transfer of oxygen from phosphorus to silicon gives rise to phosphine derivatives. Decomposition of the related phosphine oxide $(PhMe_2Si{\cdot}CH_2)_3PO$ left a neutral residue, but in all the other decompositions studied the residue was acidic.

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[3] T. Graham and R. M. C. Thompson, personal communication.

[4] Eaborn, "Organosilicon Compounds," Butterworths Scientific Publ., London, 1960, pp. 133—139; Davidson, *Chem. and Ind.*, 1960, 1107.

(*f*) The phosphate $(Me_3Si{\cdot}CH_2{\cdot}O)_3PO$ is relatively stable to heat, and 42·5% of it was recovered unchanged after 38 hours' heating at 268—295°. It is probably more stable than most simple trialkyl phosphates since no hydrogen atoms β to oxygen are available for olefin formation. Hexamethyldisiloxane was among the decomposition products.

[We had difficulty in making the phosphate $(Me_3Si{\cdot}CH_2{\cdot}O)PO(OMe)_2$, apparently because of decomposition during fractional distillation, and while we ultimately obtained it in low yield we did not examine it further. In view of the stability of tris(trimethylsilylmethyl) phosphate, it seems likely that the decomposition is a disproportionation rather than a fragmentation. Possibly the purified compound would be much more stable.]

The phosphate $(p\text{-}Me_3Si{\cdot}C_6H_4{\cdot}O)_3PO$ gave little volatile material during 42 hours at 410—310° and, while hexamethyldisiloxane was obtained in 9% yield, most of the organosilicon groups must have been incorporated into the high-boiling residue.

(*g*) The $Si{\cdot}CH_2{\cdot}CH_2{\cdot}P$ system seems to be much more stable than the $Si{\cdot}CH_2{\cdot}P$ system. Thus 73% of dimethyl 2-triethylsilylethylphosphonate was recovered after 26 hours at 222—284° (22 hours at 284°). Some decomposition occurred, to give methanol and triethylmethoxysilane.

The compound $(EtO)_3Si{\cdot}CH_2{\cdot}CH_2{\cdot}PO(OMe)_2$ decomposed much more readily, with formation of ethylene and methanol. Probably the $Si{\cdot}CH_2{\cdot}CH_2{\cdot}P$ system remained substantially intact, however, and certainly much of the silicon remained in the residue, which was a polymeric solid of very high thermal stability. It probably contained $Si{\cdot}O{\cdot}Si$, $Si{\cdot}O{\cdot}P$, and $P{\cdot}O{\cdot}P$ cross-links.

(*h*) A common feature of the decompositions of the several types of organosilicon compounds studied is the tendency of the organosilyl group to come away with oxygen initially attached to phosphorus. The direction of transfer is no doubt to be associated with the large bond energy of the Si–O bond.

[To determine whether the tendency for the transfer of oxygen was great enough to break down a simple stable organosilicon compound, we heated bis(trimethylsilyl)methane with triphenylphosphine oxide. There was no detectable formation of hexamethyldisiloxane.]

(*i*) Organosilicon-substituted phosphorus compounds of the type we have examined do not seem to differ much in stability from comparable organic phosphorus compounds.[2] The compound $Me_3Si{\cdot}CH_2{\cdot}PO(OMe)_2$, for example, is comparable in stability with the compound $n\text{-}C_5H_{11}{\cdot}PO(OMe)_2$. The siloxanes $Me_3Si{\cdot}O{\cdot}SiMe_2{\cdot}CH_2{\cdot}PO(OR)_2$ are rather less stable than the compounds $Me_3Si{\cdot}CH_2{\cdot}PO(OR)_2$, but the difference is not such as to suggest that polymers containing $Si{\cdot}CH_2{\cdot}P$ links, *e.g.*, $[{\cdot}O{\cdot}SiMe{\cdot}CH_2{\cdot}PO(OR)_2]_x$, would be notably more unstable to heat than organophosphorus compounds generally, although they are likely to be markedly less stable than simple dimethylsiloxane polymers. (The hydrolytic instability of $Si\text{–}CH_2{\cdot}P$ bonds will probably limit severely the usefulness of polymers containing them, but in a solid polymer the bonds might be protected by its insolubility.)

Tris(trimethylsilylmethyl)phosphine oxide and dimethyl 2-triethylsilylethylphosphonate are more stable than any simple organic phosphorus compounds we have examined.[2] The $Si{\cdot}CH_2{\cdot}CH_2{\cdot}P$ system is also very stable to hydrolysis,[5] and thus we prepared 2-triethylsilylethylphosphonic acid by prolonged refluxing of the dimethyl ester with concentrated hydrochloric acid.

(*j*) The modes of decomposition we have observed would not necessarily occur under other conditions, in the presence of oxygen, for example, or in contact with a metal surface. We examined briefly the effects on the ease of decomposition of dimethyl trimethylsilylmethylphosphonate of adding (i) ethylphosphonic acid, (ii) benzoyl peroxide, and (iii) glass wool. All seemed to catalyse decomposition, the acid being the most effective in

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[5] Linville, U.S.P. 2,483,615/1958; *Chem. Abs.*, 1959, **53**, 1147.

the early stages. It is probable that acids formed in initial decompositions of organic phosphorus compounds, particularly of silicon-substituted ones, have considerable influence on the subsequent decompositions, and choice of structures or conditions in which formation of acid is minimized might lead to increased stability.

EXPERIMENTAL

Preparation of Materials.—We have already described the preparations of most of the compounds used.[1] Others were made as follows.

(i) *Dialkyl trimethylsilylmethylphosphonates.* A mixture of trimethyl phosphite (37·2 g., 0·30 mole) and chloromethyltrimethylsilane (36·8 g., 0·30 mole) was refluxed (88 hr.) until the temperature of the mixture rose from 107° to 180°. Fractionation gave *dimethyl trimethylsilylmethylphosphonate* (38 g., 64·5%), b. p. 111—114°/21·5° mm., n_D^{20} 1·4350 (Found: C, 36·8; H, 8·8. $C_6H_{17}O_3PSi$ requires C, 36·7; H, 8·7%).

Bromomethyltrimethylsilane (41·3 g., 0·25 mole) was boiled for 18 hr. with a light petroleum (b. p. 60—80°) solution (300 ml.) of the salt made from sodium (5·8 g., 0·25 g.-atom) and di-n-propyl hydrogen phosphonate (41·6 g., 0·25 mole). Sodium bromide was removed by filtration, and the solvent by evaporation. The residue was distilled at reduced pressure, and then fractionated to give *di-n-propyl trimethylsilylmethylphosphonate* (24·4 g., 39%), b. p. 125—128°/10 mm., n_D^{20} 1·4331 (Found: C, 47·6; H, 9·8. $C_{10}H_{25}O_3PSi$ requires C, 47·6; H, 10·0%).

(ii) *Dialkyl pentamethyldisiloxanylmethylphosphonates.* A mixture of trimethyl phosphite (0·50 mole) and chloromethylpentamethyldisiloxane (0·50 mole) was refluxed (15 hr.) until its temperature reached 168°, and then fractionated to give *dimethyl pentamethyldisiloxanylmethylphosphonate* (67%), b. p. 130—132·5°/20—21 mm., n_D^{20} 1·4258 (Found: C, 35·7; H, 8·5. $C_8H_{23}O_4PSi_2$ requires C, 35·5; H, 8·6%).

By the method used for preparing the analogous trimethylsilylmethyl compound, *di-n-propyl pentamethyldisiloxanylmethylphosphonate*, b. p. 145—147°/10 mm., n_D^{20} 1·4272 (Found: C, 44·05; H, 9·3. $C_{12}H_{31}O_4PSi_2$ requires C, 44·1; H, 9·6%), was made in 48% yield from chloromethylpentamethyldisiloxane and di-n-propyl hydrogen phosphonate.

Di-n-pentyl pentamethyldisiloxanylmethylphosphonate, b. p. 183·5—184°/10 mm., n_D^{20} 1·4300 (Found: C, 50·5; H, 10·25. $C_{16}H_{39}O_4PSi_2$ requires C, 50·2; H, 10·3%), was similarly made in 13% yield from di-n-pentyl hydrogen phosphonate.

(iii) *Dimethyl 2-triethyl- and 2-triethoxy-silylethylphosphonate.* From dimethyl hydrogen phosphonate and triethyl- or triethoxy-vinylsilane by Linville's method[5] were prepared *dimethyl 2-triethoxysilylethylphosphonate* (23%), b. p. 158—161°/10 mm., n_D^{20} 1·4272 (Found: C, 40·2; H, 8·3. $C_{10}H_{25}O_6PSi$ requires C, 40·0; H, 8·4%), and *dimethyl 2-triethylsilylethylphosphonate* (70%), b. p. 150—153°/10 mm., n_D^{20} 1·4527 (Found: C, 47·7; H, 10·1. $C_{10}H_{25}O_3PSi$ requires C, 47·6; H, 10·0%).

(iv) *Tri-*[(p-*chlorophenyldimethylsilyl*)*methyl*]*phosphine oxide.* Phosphorus oxychloride (0·04 mole) in ether (25 ml.) was added during 1 hr. to the Grignard reagent from chloromethyl-*p*-chlorophenyldimethylsilane (0·125 mole) and magnesium (0·13 g.-atom) in ether (150 ml.). The mixture was refluxed for 17 hr. and then treated with dilute hydrochloric acid. The ether layer was separated and washed, and the solvent was removed. The residue was washed with warm 20% aqueous sodium hydroxide and then with water, and recrystallized from aqueous alcohol to give *tri-*[(p-*chlorophenyldimethylsilyl*)*methyl*]*phosphine oxide* (3·1 g., 13%), m. p. 121·5° (Found: C, 53·9; H, 6·1. $C_{27}H_{36}Cl_3OPSi_3$ requires C, 54·2; H, 6·1%).

In an earlier attempt[1] to obtain this compound by the above method but without the washing with aqueous sodium hydroxide, we isolated only di-[(*p*-chlorophenyldimethylsilylmethyl]phosphinic acid, presumably because the Grignard reagent had been inefficiently formed.

(v) *Bis*[(*dimethyl-*p-*tolylsilyl*)*methyl*]*phosphinic acid.* When we made tris[(dimethyl-*p*-tolylsilyl)methyl]phosphine oxide again by the method used before,[1] we obtained from the mother-liquors after recrystallization of the oxide, an alkali-soluble solid, which was recrystallized and found to be *bis*[(*dimethyl-*p-*tolylsilyl*)*methyl*]*phosphinic acid* (7%), m. p. 122° (Found: C, 61·7; H, 8·2. $C_{20}H_{31}O_2PSi_2$ requires C, 61·5; H, 8·0%).

(vi) *Dimethyl trimethylsilylmethyl phosphate.* Trimethylsilylmethanol (15·6 g., 0·15 mole) was added gradually to a mixture of sodium (3·5 g., 0·15 g.-atom) in ether (160 ml.) and the mixture was refluxed (5 hr.) until hydrogen evolution ceased. Dimethyl phosphorochloridate (21·7 g., 0·15 mole) was added during 20 min., and refluxing for 1 hr. was followed by filtration and removal of the ether. The residue was distilled quickly, and material of b. p. 66°/3·5 mm. to 120°/2·5 mm. was fractionated to give *dimethyl trimethylsilylmethyl phosphate* (2·1 g., 7%), b. p. 61—62°/0·4 mm., n_D^{20} 1·4158 (Found: C, 33·9; H, 8·3. $C_6H_{17}O_4PSi$ requires C, 33·9; H, 8·1%).

In several earlier attempts to make the compound by the same method, but with fractionation at 5, 10, or 20 mm. pressure, boiling points were unsteady, as though decomposition was occurring, and only impure material was obtained, along with several other fractions.

Thermal Decompositions.—The compound was heated in a " Pyrex " glass flask fitted with a water-cooled reflux condenser, the outlet from which led to a trap cooled in solid carbon dioxide and then, through a sulphuric acid bubbler or a solution of bromine in water or carbon tetrachloride, to the air. The apparatus was flushed with nitrogen before the heating, and a slow stream of the gas was maintained throughout. Usually the contents of the flask were kept boiling steadily for the time quoted, heating being adjusted as necessary. One thermometer was immersed in the liquid and another in the vapour above; the temperatures give a rough indication of the progress of decomposition, but are very dependent on the rate at which volatile material is carried away in the gas stream.

In some cases several fractionations were necessary, particularly of intermediate fractions from the initial distillations, but, for simplicity, in most cases the final results only are quoted below.

The term " loss " in the accounts denotes the difference in weight (expressed as a percentage of the weight of starting material) between the initial weight of the flask contents and the final combined weight of the contents of the flask and the cold trap. The most likely origin of the loss was inefficient trapping of gases.

Known products were identified in the usual ways by their properties and/or spectra and derivatives.

The yield (based on unrecovered starting material) of each product is calculated on the assumption that its formation is the only reaction occurring; where two or more products have groups in common this leads to the combined recoveries appearing poorer than they are. For example, in decomposition of the compound $Me_3Si\cdot CH_2\cdot PO(OMe)_2$, the compounds $Me_3Si\cdot OMe$ and $Me\cdot PO(OMe)_2$ are formed; if 100% of the former were obtained, the yield of the latter could not, in view of the number of methoxyl groups available, exceed 50%.

(a) *Dimethyl trimethylsilylmethylphosphonate.* When this compound (73·4 g.) was heated for 20 hr. the liquid temperature varied as follows:

Time (hr.)	1	4	8	12	16	20
Temp.	225°	217°	211°	210°	207°	207°

There was no loss. The cold trap contained 8·9 g. of liquid after 10½ hr. and 17·7 g. after 20 hr. The liquid, b. p. 57—59°, n_D^{20} 1·3720, was assumed to be almost all methoxytrimethylsilane (in 45% yield), since on fractionation only this compound (15·0 g., 38·5%), b. p. 54·5—56·5°, n_D^{20} 1·3680 (infrared spectrum identical with that of an authentic sample) was obtained, and more was probably held in the column.

The contents of the pyrolysis flask were fractionated to give (i) a little impure methoxytrimethylsilane, b. p. 57—60°, n_D^{20} 1·3790, (ii) dimethyl methylphosphonate (14·0 g., 30%), b. p. 181—183°, n_D^{20} 1·4125 (Found: C, 29·2; H, 7·3. Calc. for $C_3H_9O_3P$: C, 29·0; H, 7·3%) [the amount of material of b. p. 180—188°, probably almost all dimethyl methylphosphonate, was 16·3 g. (35%)], (iii) 8·0 g. of liquid of b. p. 96—110°/21·5 mm. and 4·0 g. of b. p. 69—79°/12 mm., and (iv) 0·9 g. of liquid of b. p. 111—114°/21·5 mm., n_D^{20} 1·4259, believed to be impure dimethyl trimethylsilylmethylphosphonate.

The residue (12·3 g.) left in the still became solid on cooling.

(b) *Dimethyl pentamethyldisiloxanylmethylphosphonate.* When this compound (100 g.) was heated for 10·5 hr. the liquid temperature varied as follows: fell from 238° to 194° in 10·5 hr. The loss was 1%. The cold trap contained 1 g. of a silicon-containing compound, n_D^{20} 1·3871 (probably impure methoxypentamethyldisiloxane). The residue was fractionated to give (in addition to intermediate fractions) (i) *methoxypentamethyldisiloxane* (10·3 g., 19%), b. p. 118—119°, n_D^{20} 1·3807 (Found: C, 40·4; H, 10·2. $C_6H_{18}O_2Si_2$ requires C, 40·4; H, 10·2%), (ii) 4 g. of liquid, b. p. 62—72°/20 mm., which gave two layers on cooling, (iii) dimethyl methylphosphonate (6·5 g.), b. p. 78—79°/20 mm., n_D^{20} 1·4135, (iv) 10·9 g. of liquid, b. p. 109—112°/20 mm., n_D^{20} 1·4120, (v) dimethyl pentamethyldisiloxanylmethylphosphonate (22 g., 22%), b. p.

129—132°/20 mm., n_D^{20} 1·4245, (vi) 6·7 g. of liquid, b. p. 142—144°/20 mm., n_D^{20} 1·4158, (vii) 10·0 g. of liquid, b. p. 154—170°/20 mm., n_D^{20} 1·4130—1·4220, (viii) 2·5 g. of liquid, b. p. 120°/1 mm. to 164°/0·8 mm.

The residue (3 g.), on cooling, gave an acidic, brittle, water-soluble solid.

Fraction (ii) was combined with some other small fractions which had separated into two layers, and the mixture was shaken with water. The excess of water was run off, and the lower layer was fractionated to give dimethyl methylphosphonate (3·7 g.), b. p. 63—65°/10 mm., n_D^{20} 1·4118 (Found: C, 29·5; H, 7·2. Calc. for $C_3H_9O_3P$: C, 29·0; H, 7·3%). The total yield of the compound was 10·2 g. (22%), and more of it was almost certainly present in intermediate fractions.

(c) *Diethyl pentamethyldisiloxanylmethylphosphonate.* This compound (80·0 g.) was heated for 16·5 hr.; the liquid temperature was 182° after 10 hr., and 172° after 16·5 hr. At the end the cold trap contained 1·6 g. of liquid, b. p. 131°, n_D^{20} 1·3824. This was added to the flask contents, which were fractionated to give: (i) 1·2 g. of liquid, b. p. 93—95°, n_D^{20} 1·3766 (Found: C, 46·9; H, 11·5%), containing silicon but not phosphorus, (ii) *ethoxypentamethyldisiloxane* (26 g., 50%), b. p. 133°, n_D^{20} 1·3827 (Found: C, 43·9; H, 10·6. $C_7H_{20}O_2Si_2$ requires C, 43·7; H, 10·5%) (preparation of ethyl 3,5-dinitrobenzoate, m. p. 94°, from the compound confirmed the presence of an ethoxyl group), (iii) diethyl methylphosphonate (15·0 g., 37%), b. p. 79—81°/11 mm., n_D^{20} 1·4123 (Found: C, 39·1; H, 8·5. Calc. for $C_5H_{13}O_3P$: C, 39·5; H, 8·6%).

A range of ill-defined higher-boiling fractions was also obtained. The residue (10·3 g.) gave an acidic, porous solid on cooling.

(d) *Di-n-propyl pentamethyldisiloxanylmethylphosphonate.* This compound (38·5 g.) was heated for 16 hr. The liquid temperature fell from 265° to 202° in 16 hr. The loss (1·5%) probably represented untrapped propene, since the untrapped gas decolorized bromine water. At the end of the heating the cold trap contained 1·0 g. of liquid, 0·5 g. of which boiled below room temperature (to give an inflammable gas which decolorized bromine water and was almost certainly propene), leaving a liquid which contained silicon.

Fractionation of the flask contents gave the following: (i) *pentamethyl-n-propoxydisiloxane* (10·5 g., 43%), b. p. 151·5—152·5°, n_D^{20} 1·3893 (Found: C, 46·8; H, 10·8. $C_8H_{22}O_2Si_2$ requires C, 46·6; H, 10·7%) (n-propyl 3,5-dinitrobenzoate, m. p. 74°, was made from the liquid), (ii) (8·9 g. of liquid, b. p. 98—100°/12 mm., n_D^{20} 1·4176 (Found: C, 41·7; H, 9·1; P, 10·55%), (iii) 4·4 g. of a phosphorus-containing liquid, b. p. 114—117°/12 mm., n_D^{20} 1·4130 (Found: C, 39·1; H, 9·5%). The residue (8·1 g.) gave a black acidic solid on cooling.

Neither fraction (ii) nor (iii) could be identified with the expected di-n-propyl methylphosphonate (lit.,[6] b. p. 105—106°/12 mm., n_D^{18} 1·4082. Calc. for $C_7H_{17}O_3P$: C, 46·7; H, 9·5; P, 17·2%), but they may have been azeotropes containing this compound.

Bands at 7·67 and 9·4—10·2 μ for fraction (ii) were consistent with the presence of P=O and P–O–C links.

(e) *Di-n-propyl trimethylsilylmethylphosphonate.* This compound (23·6 g.) was heated for 22 hr.; the temperature of the liquid was 243° after 0·75 hr., 222° after 12 hr., and 215° after 21 and 22 hr. Untrapped gas decolorized bromine water, and the overall loss, 1·0 g., probably represented propene formation (13%).

Some of the contents of the cold trap boiled below room temperature, and the residue (2·2 g.; b. p. 98—102°) was added to the contents of the reaction flask. Fractionation gave: (i) trimethyl-n-propoxysilane (3·9 g., 31·5%), b. p. 100—102°, n_D^{20} 1·3841, (ii) 7·3 g. of liquid, b. p. 95—96°/12 mm., n_D^{20} 1·4165, (iii) 6·0 g. of liquid, b. p. 98—100°/12 mm., n_D^{20} 1·4182. The residue (2·0 g.) set to an acidic solid on cooling. Near the end of the distillation some crystals collected in the still-head; they quickly liquefied and inflamed when exposed to the air.

Fractions (ii) and (iii) are similar in physical properties to fraction (ii) obtained from di-n-propyl pentamethyldisiloxanylmethylphosphonate, but analysis of fraction (ii) in the present case gave different results (C, 32·3; H, 7·75; P, 9·1%), though it is possible that one or other of the analyses was at fault (Calc. for di-n-propyl methylphosphonate: C, 46·7; H, 9·5; P, 17·2%).

(f) *Di-n-butyl trimethylsilylmethylphosphonate.* This compound (14·0 g.) was heated for 12 hr.; the liquid temperature rose from 243° to 370° in 12 hr. When heating was stopped the contents of the flask set to an infusible acidic, cream-coloured solid (5·9 g.). The contents of

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[6] Kosolapoff, " Organophosphorus Compounds," John Wiley and Sons, Inc., New York, 1950, p. 149.

the cold trap weighed 2·0 g. after 9 hr. and 7·2 g. after 12 hr. They were distilled to give but-1-ene (4·2 g., 75%) and hexamethyldisiloxane (3·0 g., 73%), b. p. 99—100°. The loss (6·5%) probably represents untrapped butene (16%).

(g) *Di-n-butyl pentamethyldisiloxanylmethylphosphonate.* When this compound (11·0 g.) was heated, the liquid temperature was 272° after 10 min., 204° after 30 min., 231° after 3 hr., and 224° after 7 hr. At the end of this time the cold trap contained 0·15 g. of liquid, some of which was but-1-ene; the loss (4%) probably also represented butene. Fractionation of the contents of the flask gave *n-butoxypentamethyldisiloxane* (4·25 g., 62%), b. p. 172°, n_D^{20} 1·3938 (Found: C, 48·8; H, 11·1. $C_9H_{24}O_2Si_2$ requires C, 49·0; H, 11·0%). The presence of an n-butoxyl group was confirmed by preparation of n-butyl 3,5-dinitrobenzoate, m. p. 64·5°.

From one small-scale decomposition (7 hr.) of di-n-butyl pentamethyldisiloxanylmethylphosphonate, the volatile silicon compound obtained (51%) had b. p. 140—142°, n_D^{20} 1·3923 (Found: C, 49·1; H, 10·9%), and possibly contained a rearranged butoxyl group. In other similar experiments, however, only the compound of b. p. 172° was obtained.

(h) *Di-n-pentyl trimethylsilylmethylphosphonate.* This compound (7·1 g.) was heated for 2 hr.; the liquid temperature was 270° after 0·5 hr., 274° after 1 hr., and >360° after 2 hr. The contents of the flask (3·4 g.) gave a sticky, pale yellow glass on cooling. The loss was 6%. The cold trap contained 3·3 g. of liquid; fractionation gave pent-1-ene (2·0 g., 62%), b. p. 29—31°, n_D^{20} 1·3720 (the infrared spectrum showed that isomeric pentenes were absent), and left a liquid residue (0·3 g.), b. p. 98—100°, n_D^{20} 1·3800, which was shown by means of its infrared spectrum to be fairly pure hexamethyldisiloxane (16%).

(i) *Di-n-butyl (phenyldimethylsilyl)methylphosphonate.* This compound (19·5 g.) was heated for 10·5 hr. During the first few minutes the liquid temperature rose to 310°, but fell to 210° in 10 hr. The loss (3·2 g., 17%) was unusually high, and at most only about half of it could represent butene.

The cold trap contained 4·9 g. of silicon-free liquid; 4·1 g. (54%) of it was pure but-1-ene (infrared spectrum) and the remainder, b. p. 80—85°, n_D^{20} 1·4895, mainly benzene (18%).

Fractionation of the contents of the reaction flask gave benzene (2·2 g., 48%) b. p. 80°, n_D^{20} 1·5000. The residue cooled to an acidic, viscous, black liquid.

(j) *Di-n-butyl (dimethyl-*p*-tolylsilyl)methylphosphonate.* This compound (13·4 g.) was heated for 15·5 hr. The liquid temperature was 300° after 0·5 hr. and 1·5 hr., fell to 244° in 10 hr., and rose again to 360° after 15·5 hr. The loss (15%) was unusually large, as in the preceding experiment, and only about half of it could have been butene.

From the cold trap but-1-ene (3·5 g., 83%) was distilled to leave toluene (1·9 g.), b. p. 110°, n_D^{20} 1·4940, which appeared, from its ultraviolet absorption spectrum to be 90% pure. Fractionation of the contents of the reaction flask gave more toluene (0·5 g., total 64%), b. p. 110°. The residue set to an acidic, brittle solid.

(k) *Di-n-butyl (*p*-chlorophenyldimethylsilyl)methylphosphonate.* When this compound (4·7 g.) was heated for 10 hr., the liquid temperature was 314° after 1 hr. and 170° after 8·5 and 10 hr. The cold trap contained but-1-ene (0·9 g., 64%). Fractionation of the contents of the flask gave chlorobenzene (0·6 g., 43%), b. p. 132—133°, and an acidic solid. The percentage loss (19%) was large, but represents only 0·9 g.

(l) *Tris(trimethylsilylmethyl) phosphine oxide.* When this compound (12·5 g.) was heated for 22 hr., the liquid temperature was 261° after 0·5 hr., 229° after 1 hr., 217° after 10 hr., 218° after 18 hr., and 221° after 22 hr. The loss (0·8%) was small. The cold trap contained hexamethyldisiloxane (2·0 g., 30%), b. p. 100°, n_D^{20} 1·3780, almost pure (infrared spectrum). The flask contents were fractionated to give (i) 1·0 g. of a yellow liquid, b. p. 158—160°, which deposited crystals, (ii) 0·9 g. of silicon-containing liquid, b. p. 68—70°/10 mm., which fumed in the air, (iii) 0·9 g. of liquid, b. p. 100—104°/10 mm., (iv) 1·0 g. of liquid, b. p. 165—168°/10 mm., all becoming brown readily.

(m) *Tris(trimethylsilylmethyl) phosphate.* This compound (10·0 g.) was heated for 38 hr., during which the liquid temperature rose from 268° to 295°. The cold trap contained 0·9 g. of a silicon-containing liquid, b. p. 96—113°, n_D^{20} 1·3940; this was not impure hexamethyldisiloxane, since strong absorption at 13·24 μ was absent. Fractionation of the flask contents gave the original compound (4·25 g., 42·5%), b. p. 130—135°/5 mm., n_D^{20} 1·4241, somewhat impure. The residue was acidic.

(n) *Tris-(*p*-trimethylsilylphenyl)phosphate.* When this compound (11·1 g.) was heated for 42 hr., the liquid temperature was 410° after 0·5 hr., 350° after 2 hr. and 21 hr., 315° after 27 hr., 320° after 31 hr., and 310° after 42 hr. The loss (1·5%) was small. The cold trap contained 0·3 g. of fairly pure hexamethyldisiloxane (9%) (infrared spectrum). Fractionation of the contents of the flask gave (i) 0·2 g. of liquid, b. p. 63°/10 mm., n_D^{20} 1·4870, and (ii) 0·8 g. of liquid, b. p. 107°/10 mm. There was no fraction at the b. p. (245°/11 mm.) of triphenyl phosphate. The solid residue (7·5 g.) gave no crystals. The infrared spectrum of fraction (ii) had peaks at 8·0 and 11·93 μ consistent with the presence of an Si–Me bond, and one at 7·91 μ consistent with the presence of a P=O bond.

(o) *Dimethyl 2-triethylsilylethylphosphonate.* When this compound (75 g.) was heated for 26 hr., the liquid temperature rose from 222° to 284° during the first 4 hr. and then remained constant. The loss (4·5%) was small. The cold trap contained 1·1 g. of material, 0·1 g. of which boiled below room temperature as an inflammable gas which decolorized bromine water. The residue was methanol (1·0 g., 20%), b. p. 63—64·5° (m. p. of 3,5-dinitrobenzoate, 108°). Fractionation of the contents of the flask gave 1·6 g. of liquid, b. p. 141—143°, n_D^{20} 1·4120, assumed to be triethylmethoxysilane (14%) (lit.,[7] b. p. 141·5°, n_D^{20} 1·4129), and unchanged starting material (54·7 g., 73%), b. p. 150—153°/10 mm., n_D^{20} 1·4538. The residue was an acidic liquid.

(p) *Dimethyl 2-triethoxysilylethylphosphonate.* This compound (40·1 g.) was heated (23 hr.) until a solid appeared in the hot mass. The liquid temperature was 261° after 23 hr. There was a 4% loss. During the heating, the gas emerging from the cold trap was passed into a solution of bromine in carbon tetrachloride, and from this 1,2-dibromoethane (4·7 g.), b. p. 132°, m. p. 9·5°, was obtained, so that at least 0·8 g. (9%) of ethylene had been formed. The cold trap contained a liquid of b. p. 4—6°, which decolorized bromine water, and methanol (2·0 g., 23%), b. p. 63—65° (m. p. of 3,5-dinitrobenzoate, 107°). The liquid in the reaction flask was decanted from the solid and fractionated to give (i) 1·1 g. of liquid, b. p. 60—90°, n_D^{20} 1·361 (probably mainly methanol), and (ii) 0·9 g. of liquid, b. p. 90—140°, n_D^{20} 1·3974; after removal of these fractions the residue in the pyrolysis flask consisted of a white porous solid (Found: C, 25·2; H, 5·4%) and a small proportion of a translucent rubbery material (Found: C, 28·4; H, 6·2%), which gave the white porous solid when heated. (In view of the high thermal-stability and flame-resistance of the polymers, the observed carbon and hydrogen contents would best be regarded as minimum values.) The solid charred slowly in a Bunsen flame, but did not burn, and retained its shape. It was probably a highly cross-linked polymer containing Si–O–Si, Si–O–P, and P–O–P links; a polymer made up of $[(HO)(MeO)P(O){\cdot}CH_2{\cdot}CH_2{\cdot}Si(OEt)O]$ units, for example, would contain C, 28·3; H, 6·2%. The total amount of polymeric material obtained was 28 g., which represents 70% of the weight of compound taken.

Effects of Additives on the Decomposition of Dimethyl Trimethylsilylmethylphosphonate.—Similar samples of the phosphonate were placed in each of four small test tubes; one was left pure, a little ethylphosphonic acid was added to the second, a little benzoyl peroxide to the third, and some glass wool to the fourth. The tubes were fitted with thermometers having their bulbs below the liquid surface, flushed out with nitrogen, and closed with cotton wool plugs. They were placed side by side in an oil bath, the temperature of which was raised until the liquid without additive was refluxing gently on the walls of the tube above the bath surface.

TABLE 2.

Reflux temperature and colour of $Me_3Si{\cdot}CH_2{\cdot}PO(OMe)_2$ alone and with additives.

Time	Additive			
(min.)	None	$Et{\cdot}PO(OH)_2$	$(Ph{\cdot}CO{\cdot}O)_2$	Glass wool
20	212°	196° [a]	207°	209°
35	209	193 [a]	199	200
	Yellow	Yellow	Brown	Yellow
80	201	196	197	198
	Yellow	Yellow	Dark brown	Brown
120	198	194	191	192
	Yellow	Yellow	Dark brown	Brown

[a] Vigorous refluxing.

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[7] Dolgov, Kharitonov, and Voronkov, *Zhur. obshchei Khim.*, 1954, **24**, 1178.

The temperature was subsequently adjusted to maintain this reflux, which meant that more vigorous refluxing was occurring in the other tubes.

The results are shown in Table 2. Because of the adjustment of the bath temperature only the boiling temperatures relative to one another are significant, these giving an indication of the extent of decomposition. It appeared that all the additives catalysed decomposition. The ethylphosphonic acid was the most effective in the early stages, but the differences decreased later, probably as acid formed in the other systems. Loss of volatile material, however, would also contribute to the levelling-out.

Lack of Interaction of Triphenylphosphine Oxide and Bis(trimethylsilyl)methane.—No hexamethyldisiloxane was detected when (i) a mixture of bis(trimethylsilyl)methane (4 g.) and triphenylphosphine oxide (7 g.) was refluxed in nitrogen for 3·5 hr., or (ii) a mixture of the organosilane (0·5 g.) and the phosphine oxide (0·9 g.) was heated in a sealed tube at 400° for 5·5 hr.; in the latter case decomposition occurred, but no liquid product boiled below 130°.

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