Some [Tris(trimethylsilyl)methyl]phosphorus Derivatives

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Treatment of $Li[C(SiMe_3)_3]$ with PPh_2Cl gave the phosphine $P[C(SiMe_3)_3]Ph_2$, which, in spite of the steric crowding caused by the silicon ligand, was readily converted into the phosphonium salts $[P\{C(SiMe_3)_3\}Ph_2H]I$ and $[P\{C(SiMe_3)_3\}Ph_2Me]I$; the latter on heating gave the ylid $MePh_2P{=}C(SiMe_3)_2$. In methanol at room temperature the phosphine $P[C(SiMe_3)_3]Ph_2$ readily loses one Me_3Si group to give $P[CH(SiMe_3)_2]Ph_2$; the remaining Me_3Si groups are lost successively, with decreasing ease, giving finally PPh_2Me. These Si–C bond cleavages are catalysed by acid but inhibited by base, and it is suggested that the initial step is protonation of the phosphine. The quaternary salt $[P\{C(SiMe_3)_3\}Ph_2Me]I$ successively loses its Me_3Si groups very readily in methanol, ultimately to give $[PPh_2Me_2]I$.

Organosilicon compounds with the very bulky tris(trimethylsilyl)methyl group attached to silicon have been shown to have highly unusual properties.[1] The zinc, cadmium, and mercury compounds $M[C(SiMe_3)_3]_2$, containing two such ligands, are also unusual in that they are exceptionally unreactive,[2,3] the most impressive illustration being that the zinc compound can be steam distilled unchanged.[2] It is thus of interest to examine the effects of attachment of this very bulky ligand to other metal and metalloid centres, and some studies of its derivatives containing boron,[4] germanium,[5–7] and tin [5,8] have been reported. We now describe the properties of some compounds in which the ligand is attached to phosphorus. While this work was in progress, the preparation of $P[C(SiMe_3)_3]Cl_2$ and a range of compounds of the type $P[C(SiMe_3)_3]RCl$, and their very interesting conversions into the species $(Me_3Si)_2C{=}PCl$ and $(Me_3Si)_2C{=}PR$ on heating, were described.[9] The preparation of $P[C(SiMe_3)_3]H_2$ has also been reported.[9a]

Results and Discussion

Preparations.—The reaction between $Li[C(SiMe_3)_3]$ and PPh_2Cl in diethyl ether–tetrahydrofuran (thf) gave the expected phosphine $P[C(SiMe_3)_3]Ph_2$ as a solid. Treatment of this with aqueous hydrogen iodide gave the quaternary salt $[P\{C(SiMe_3)_3\}Ph_2H]I$, and treatment with MeI in toluene correspondingly gave $[P\{C(SiMe_3)_3\}Ph_2Me]I$. Heating of the latter salt at 110 °C gave, by loss of $SiMe_3I$, the ylid $MePh_2P{=}C(SiMe_3)_2$, several analogues of which are known (see, *e.g.*, refs. 10 and 11). The observed loss of trimethylsilyl halide from a (trimethylsilylmethyl)phosphonium salt (while occurring in this case at an unusually low temperature, possibly reflecting relief of steric strain) is well precedented, but is commonly followed by interaction of the formed ylid with the starting material; *e.g.*[11] equations (i) and (ii). The second

$$[P(CH_2SiMe_3)Ph_3]Cl \rightleftharpoons Ph_3P{=}CH_2 + SiMe_3Cl \qquad \text{(i)}$$

$$Ph_3P{=}CH_2 + [P(CH_2SiMe_3)Ph_3]Cl \rightleftharpoons Ph_3P{=}CHSiMe_3 + [PPh_3Me]Cl \qquad \text{(ii)}$$

step in such a sequence results in the formation of a more from a less silyl-substituted ylid; in our case the fully silyl-substituted ylid is formed in the first step.

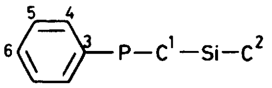
For the cleavage studies described below the related compounds $P[CH(SiMe_3)_2]Ph_2$ and $P(CH_2SiMe_3)Ph_2$ were prepared from PPh_2Cl, by use of $Li[CH(SiMe_3)_2]$ and $Mg(CH_2SiMe_3)Cl$, respectively. Both were converted into the corresponding quaternary salts by treatment with methyl iodide or aqueous hydrogen iodide.

As described by Issleib *et al.*,[9a] $P[C(SiMe_3)_3]Cl_2$ was made from $Li[C(SiMe_3)_3]$ and PCl_3 and reduced to $P[C(SiMe_3)_3]H_2$. These products are remarkable in that they can be recrystallized from MeOH.

N.m.r. Spectra.—The n.m.r. spectra (Table 1) confirm the assumed structures of the phosphines and phosphonium salts. As the number of trimethylsilyl substituents *n* in the phosphines $P[C(SiMe_3)_nH_{3-n}]Ph_2$ is increased from 1 to 3, (*a*) the ^{31}P resonance moves to lower field, (*b*) the resonance of C^1 in the ^{13}C spectrum moves to higher field, and (*c*) the coupling constants $^1J(PC^1)$ and $^1J(PC^3)$ increase. The first and third of these trends were observed in the series $P(CMe_nH_{3-n})Ph_2$ and associated with changes in C–P–C bond angles as the size of the alkyl group increases.[12] Assignments of the ^{13}C spectra of diphenylphosphonium salts were made by analogy with those in previous studies, in which it was assumed that the shift of the *meta*-carbon is least affected by changes elsewhere in the molecule.[13–15] As expected, the largest changes on quaternization are observed in the coupling constants $J(PC^1)$ and $J(PC^3)$: by comparison with data in the literature [13] it is possible that the coupling constant is negative in the phosphine and positive in the phosphonium salt; if this is the case the (negative) value for $J(PC^1)$ in the highly congested $P[C(SiMe_3)_3]Ph_2$ is exceptionally large. N.m.r. parameters for phosphonium salts are much less sensitive than those of phosphines to changes in the number of trimethylsilyl substituents in the alkyl group, perhaps indicating that there is less scope for adjustment in compounds of four-co-ordinate phosphorus to stereochemical constraints. The directly bound phosphorus–hydrogen coupling constants (508 Hz) are close to those in $[PPh_3H]^+$ or $[PPh_2(cyclo\text{-}C_6H_{11})H]^+$,[16] but much larger than those in $[PBu^t_3H]^+$ (436 Hz) or $[P(cyclo\text{-}C_6H_{11})_3H]^+$ (445 Hz), where the low values have been ascribed to steric effects which reduce the *s* component in the P–H bonds.[17] For most phosphines, including $P[CH(SiMe_3)_2]Ph_2$ and $P(CH_2SiMe_3)Ph_2$, the ^{31}P resonance moves to lower field on protonation; for $P[C(SiMe_3)_3]Ph_2$, as for PBu^t_3, the shift is to higher field. The coupling constant $^1J(C^1H)$ in the phosphine $P[CH(SiMe_3)_2]Ph_2$ (108 Hz) is considerably less than the normal value for sp^3-hybridized carbon. The coupling constant $^1J(CH)$ is even smaller in tris(trimethylsilyl)methane, *viz.* 101 Hz.[18]

Mass Spectra.—The phosphines $P[C(SiMe_3)_nH_{3-n}]Ph_2$ give strong peaks corresponding to parent ions (M^+) and ions

Table 1. N.m.r. data



Compound	^{1}H[a]				^{31}P[b]	^{13}C[c]					
	Solvent[d]	C^1H_{3-n}	C^2H_3	Ph		C^1	C^2	C^3	C^4	C^5	C^6
$P[C(SiMe_3)_3]Cl_2$	C_6H_6	—	0.6 (d,2)	—	233	23.3 (d, 103.8)	4.5 (d, 1)				
$P[C(SiMe_3)_3]H_2$	C_6H_6	—	0.5 (s)	—	−138 (t)[e]	4.6 (d, 56)	1.9 (d, 1)				
$P[C(SiMe_3)_3]Ph_2$	CH_2Cl_2-CCl_4	—	0.4 (s)	7.8—8.1	11.4	9.5 (d, 71.7)	5.8 (s)	139.2 (d, 27.5)	136.3 (d, 25.9)	127.5 (d, 9.1)	128.6 (s)
$P[CH(SiMe_3)_2]Ph_2$[f]	C_6D_6	1.3 (d, 4)	0.1 (s)	6.9—7.7	−15.4	10.6 (d, 50.4)	1.6 (d, 3.0)	140.9 (d, 18.3)	133.3 (d, 22.8)	127.4 (d, 4.5)	126.4 (s)
$P(CH_2SiMe_3)Ph_2$[g]	C_6D_6	1.5 (s)[h]	0.2 (s)[h]	7.1—7.7	−21.9	14.6 (d, 30.5)	−0.2 (d, 1)	141.4 (d, 15.3)	132.3 (d, 19.8)	128 (s)	128.0 (s)
$[P\{C(SiMe_3)_3\}Ph_2H]I$[i]	$CDCl_3$	—	0.4 (s)	7.5—8.5	−0.5	5.7 (d, 18.4)	2.1 (s)	122.4 (d, 81)	133.0 (d, 10.7)	129.7 (d, 13.7)	133.7 (s)
$[P\{CH(SiMe_3)_2\}Ph_2H]I$[j]	CH_2Cl_2	2.78 (dd)	0.4 (s)	7.1—8.2	−0.3	5.0 (d, 17.6)	1.4 (d, 2.9)	121.7 (d, 81)	132.4 (d, 11.8)	129.0 (d, 13.2)	133.0 (d, 2.9)
$[P(CH_2SiMe_3)Ph_2H]I$[k]	CH_2Cl_2	2.46 (dd)	0.2 (s)	7.5—8.4	−3.9	6.5 (d, 36.8)	0.6 (d, 2.9)	119.2 (d, 83.8)	132.4 (d, 11.8)	129.3 (d, 11.8)	133.8 (s)
$[PPh_2MeH]I$[l]	$CDCl_3$	2.74 (dd)	—	7.4—8.4	−5.6	15.9 (d, 73.5)	—	133.8 (d, 100)	130.4 (d, 10.3)	129.1 (d, 11.8)	132.2 (d, 2.9)
$[P\{C(SiMe_3)_3\}Ph_2Me]I$[m]	$CHCl_3$	—	0.6	7.4—8.1	26.3	2.0 (d, 38.1)[n]	7.1 (s)	124.6 (d, 81)	133.5 (d, 10.7)	129.8 (d, 12.2)	134.3 (s)
$[P\{CH(SiMe_3)_2\}Ph_2Me]I$[o]	$CDCl_3$	3.0 (d, 23)	0.2	7.5—8.2	24.1	8.3 (d, 26.5)	2.7 (s)	125.0 (d, 85.3)	132.0 (d, 11.8)	129.9 (d, 11.8)	133.7 (s)
$[P(CH_2SiMe_3)Ph_2Me]I$[p]	$CDCl_3$	2.78 (d, 19)	0.14	7.5—8.1	23.2	9.4 (d, 38.3)	−0.9 (s)	120.9 (d, 87)	130.7 (d, 10.3)	128.5 (d, 13.2)	132.8 (s)
$[PPh_2Me_2]I$	$CDCl_3$	2.83 (d, 13)	—		20.4	8.1 (d, 55.9)	—	121.6 (d, 87)	131.7 (d, 10.3)	129.6 (d, 11.8)	134.2 (d, 2.9)

[a] Chemical shifts as δ values. Solvent peaks assumed to be at 7.25 ($CHCl_3$), 7.30 (C_6H_6), or 5.35 p.p.m. (CH_2Cl_2). [b] In p.p.m. downfield (positive) from 85% H_3PO_4. Phosphines in C_6D_6 and phosphonium salts in $CDCl_3$. [c] In p.p.m. downfield from $SiMe_4$; P–C coupling constants (Hz) in parentheses. Phosphines in C_6D_6 and phosphonium salts in $CDCl_3$, except for $[PPh_2MeH]I$ in $(CD_3)_2SO$. [d] For ^{1}H n.m.r. only. [e] *J*(PH) 188 Hz. [f] *J*(CH) 119 ($SiMe_3$), 160 (Ph), and 109 (CH) Hz; *J*(PCH) 5 Hz. [g] *J*(CH) 117 ($SiMe_3$) and 121 (CH_2); ^{4}*J*(PCSiCH) 1 Hz. [h] B. E. Cooper and W. J. Owen, *J. Organomet. Chem.*, 1970, **21**, 329. [i] *J*(PH) 503 Hz. [j] δ(P*H*) 10.2 (dd); *J*(PH) 508, *J*(PCH) 24, *J*(*H*PCH) 12, and *J*(CH) (Me_3Si) 121 Hz. [k] δ(P*H*) 10.2 (dt); *J*(PH) 508, *J*(PCH) 22, *J*(HPCH) 9, *J*(CH) 119 (Me_3Si), and 122 Hz (CH_2). [l] δ(P*H*) 10.1 (dq), *J*(PH) 520. [m] δ(PC*H*$_3$) 3.0 (d), *J*(PCH) 11 Hz; δ(P*C*H$_3$) 17.4, *J*(PC) 56.4 Hz. [n] Assignment doubtful: peak may be obscured by C^2 signal. [o] δ(PC*H*$_3$) 2.85 (d), *J*(PCH) 12.6 Hz. [p] δ(PC*H*$_3$) 2.73, *J*(PCH) 13 Hz; δ(P*C*H$_3$) 9.8, *J*(PC) 57.4 Hz.

Table 2. Reaction of $P[C(SiMe_3)_3]Ph_2$ with MeOH (at *ca.* 21 °C) to give $P[C(SiMe_3)_nH_{3-n}]Ph_2$

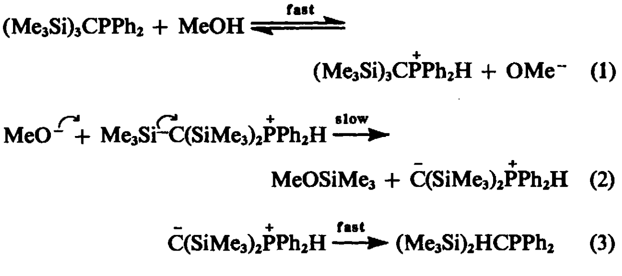
	Product composition (%)			
t/h	$n =$ 3	2	1	0
0.5	28	72		
24			90	10
46			80	20
68			76	24
168			44	56
216			36	64
312			27	73

$[M - H]^+$, $[M - Me]^+$, and $[M - SiMe_3]^+$ together with peaks having m/e 185, 183, and 135. The ions arising by loss of H from the parent are probably similar to those found in the mass spectrum of triphenylphosphine.[19] The mass spectra obtained by heating samples of the phosphonium salts $[P\{CH(SiMe_3)_2\}Ph_2H]I$ and $[P(CH_2SiMe_3)Ph_2H]I$ in the probe of the instrument (see Experimental section) clearly correspond to products formed by elimination of hydrogen iodide (M^+ 344 and 272, respectively). The compound $[P\{CH(SiMe_3)_2\}Ph_2Me]I$ also decomposed in the probe (at 170 °C) to give $MePh_2P{=}C(SiMe_3)_2$ and hydrogen iodide.

Cleavage Studies.—The phosphine $P[C(SiMe_3)_3]Ph_2$ decomposed when an attempt was made to recrystallize it from methanol. A solution of this phosphine in methanol at room temperature was shown by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy (see Table 2) to contain $P[C(SiMe_3)_3]Ph_2$ and $P[CH(SiMe_3)_2]Ph_2$ in 28 : 72 ratio after 0.5 h; after 24 h only $P(CH_2SiMe_3)Ph_2$ and PPh_2Me were present, in 90 : 10 ratio, the former subsequently being converted progressively and relatively slowly into the latter. The presence of 0.05 mol dm^{-3} CF_3CO_2H in the methanol increased the rate of cleavage, so that after 0.5 h no $P[C(SiMe_3)_3]Ph_2$ remained and $P[CH(SiMe_3)_2]Ph_2$ and $P(CH_2SiMe_3)Ph_2$ were present in 17 : 83 ratio, and after 24 h only $P(CH_2SiMe_3)Ph_2$ and PPh_2Me were present, in 74 : 26 ratio. (In acidic media both protonated and unprotonated phosphines are present, and the quoted ratios are those of unprotonated species as given by ^{31}P n.m.r. spectroscopy after neutralization of the solutions.)

A solution of the phosphonium salt $[P\{C(SiMe_3)_3\}Ph_2H]I$ in methanol contained (after neutralization) the compounds $P[C(SiMe_3)_nH_{3-n}]Ph_2$ with $n = 2, 1,$ and 0 in 34 : 48 : 18 ratio after only 15 min, the hydrogen iodide acting as a catalyst as expected, while a solution of the methiodide salt $[P\{C(SiMe_3)_3\}Ph_2Me]I$ after only 5 min contained only $[P(CH_2SiMe_3)Ph_2Me]I$ and $[PPh_2Me_2]I$ in 27 : 73 ratio, and only the latter salt was present after 15 min. In contrast, $P[C(SiMe_3)_3]Ph_2$ was unchanged after 168 h in an 0.05 mol dm^{-3} solution of NaOMe in MeOH, or after this same time in Bu^{t}OH. While our results do not demonstrate that the cleavages of the phosphonium ions are catalyzed by base (the cleavages being so fast in methanol alone that the base catalysis cannot be satisfactorily detected by the procedure we used), the analogous cleavages of the salts $[P(CH_2SiMe_3)Me_3]Cl$ and $[P(CH_2SiMe_3)Ph_3]Br$ by water are known to be strongly accelerated by base.[20,21]

It is evident that all three Me_3Si groups of $P[C(SiMe_3)_3]Ph_2$ are cleaved successively by methanol, the ease of reaction falling with the number of such groups remaining. The initial step appears to be protonation at phosphorus in the rapidly established reversible process (1) of the Scheme (lying far over to the left-hand side), and presumably a nucleophile, most simply OMe^-, then attacks at silicon, in a slow step (2), to give the ylid $P[C(SiMe_3)_2]Ph_2H$ which subsequently rapidly isomerizes (no doubt *via* proton transfers to and from the solvent) to $P[CH(SiMe_3)_2]Ph_2$ in step (3). Similar processes then operate for removal of the remaining Me_3Si groups.



$$(Me_3Si)_3CPPh_2 + MeOH \overset{fast}{\rightleftharpoons} (Me_3Si)_3C\overset{+}{P}Ph_2H + OMe^- \quad (1)$$

$$MeO^- + Me_3Si\text{–}C(SiMe_3)_2\overset{+}{P}Ph_2H \xrightarrow{slow} MeOSiMe_3 + \overset{-}{C}(SiMe_3)_2\overset{+}{P}Ph_2H \quad (2)$$

$$\overset{-}{C}(SiMe_3)_2\overset{+}{P}Ph_2H \xrightarrow{fast} (Me_3Si)_2HCPPh_2 \quad (3)$$

Scheme.

The observed catalysis by acid and the inhibition by NaOMe (which prevents the protonation at phosphorus) are consistent with this Scheme, as is the rapid cleavage of the quaternary methiodide salts. The absence of any reaction between $P[C(SiMe_3)_3]Ph_2$ and Bu^{t}OH can be understood in terms of the lower acidity of this alcohol, implying a smaller degree of protonation of the phosphine, but steric factors may also be of importance. It is noteworthy that the Scheme is consistent with the ease of cleavage of the $Me_3Si\text{–}C$ bonds of ylids such as $Me_3P{=}CHSiMe_3$ by water or alcohols,[11,20,22] and with catalysis of the reaction by acid,[20] since initial protonation at the negative carbon centre in the ylid gives the phosphonium ion, such as $[Me_3PCH_2SiMe_3]^+$.

The decrease in the rate of cleavage of the $Me_3Si\text{–}C$ bonds with the decrease in the value of n in $P[C(SiMe_3)_nH_{3-n}]Ph_2$ is of interest, and it is appropriate to consider the factors likely to affect this sequence. The observed rate in each case will be determined by the degree of protonation of the relevant phosphine in step (1) and by the rate constant for the subsequent cleavage step (2). Increase in n could be expected to favour the protonation as a result of the increased release of electrons (by inductive effects and possibly by hyperconjugative interaction with the vacant d orbitals of the positively charged phosphorus atom) from the $Me_3Si\text{–}C$ bonds, but this should be countered by an increase in steric strain in the phosphonium salt and also in the steric hindrance to its solvation. Again the ease of the cleavage step (2) could be expected to increase with increasing stabilization of the carbanion centre in the ylid $P[C(SiMe_3)_nH_{2-n}]Ph_2H$ by the Me_3Si groups [compare the high acidity of $(Me_3Si)_3CH$ [23]], and with increasing release of steric strain upon cleavage. However, for the series of compounds $C(SiMe_3)_nH_{3-n}Ph$, the ease of base cleavage of the $Me_3Si\text{–}C$ bonds falls steeply with increase in n,[24] but it is conceivable that the steric effects would act in the opposite direction in the highly reactive phosphonium ions $[P\{C(SiMe_3)_nH_{3-n}\}Ph_2H]^+$. (The fact that some of the product having $n = 1$ is present along with that having $n = 0$ after 5 min in a solution in methanol initially containing the ion with $n = 3$ indicates that the cleavage of the last $Me_3Si\text{–}C$ bond in the phosphonium ion with $n = 1$ is not markedly faster than that of the bonds in the ions with $n = 2$ or 3, and may be slower.)

The absence of cleavage of the $Me_3Si\text{–}C$ bonds of $P[C(SiMe_3)_3]Cl_2$ and $P[C(SiMe_3)_3]H_2$ on recrystallization from MeOH can be attributed to a lower degree of protonation of the phosphorus centre.

Experimental

As far as possible, air and moisture were excluded from all reactions. Mass spectra were measured at 70 eV (*ca.* 1.12 ×

10^{-17} J). Tris(trimethylsilyl)methyl-lithium, $Li[C(SiMe_3)_3]$ was made in Et_2O–thf from $(Me_3Si)_3CH$ and LiMe (made from MeCl) as previously described.[5]

Diphenyl[*tris*(*trimethylsilyl*)*methyl*]*phosphine*.—A solution of $Li[C(SiMe_3)_3]$ (7.4 mmol) in thf (30 cm^3) and diethyl ether (8 cm^3) was treated with ethoxytrimethylsilane (3 mmol) to remove any excess of methyl-lithium. The resulting solution was then added slowly during 0.5 h to freshly distilled chlorodiphenylphosphine (1.8 cm^3, 10 mmol) in ether (20 cm^3) and the mixture was heated under reflux for 2 h. After removal of solvent, the residue was extracted with pentane, and the *product* separated as crystals from the extract after concentration. The crystals were washed rapidly with cold ethanol. Yield 48%, m.p. 189—191 °C (Found: C, 63.3; H, 8.3. $C_{22}H_{37}PSi_3$ requires C, 63.4; H, 8.9%).

[*Bis*(*trimethylsilyl*)*methyl*]*diphenylphosphine*.—A solution containing n-butyl-lithium (12.5 mmol) and *NNN'N'*-tetramethylethylenediamine (12.5 mmol) in hexane (8.3 cm^3) at 0 °C was treated with bis(trimethylsilyl)methane (2 g, 12.5 mmol). After standing overnight and cooling to −78 °C, PPh_2Cl (12.5 mmol) in ether (10 cm^3) was added and the mixture stirred for 2 h first at −78 °C and then at 20 °C. The solvent was evaporated in vacuum and the residue was extracted with pentane; white crystals of the *phosphine* were obtained on cooling the pentane solution. Yield 57%, m.p. 90—93 °C (Found: C, 65.6; H, 8.1. $C_{19}H_{29}PSi_2$ requires C, 66.2; H, 8.4%).

Diphenyl(trimethylsilylmethyl)phosphine was made from $Mg(CH_2SiMe_3)Cl$ and PPh_2Cl.[25]

Diphenyl[*tris*(*trimethylsilyl*)*methyl*]*phosphonium Iodide*.—The phosphine $P[C(SiMe_3)_3]Ph_2$ (0.35 g, 0.84 mmol) was suspended in warm aqueous HI (4 cm^3, 18 mmol) for about 1 min, and the solution was quickly cooled. The white *crystals* were washed first with glacial acetic acid and then with toluene. Yield 62%, m.p. 152—154 °C (Found: C, 48.2; H, 6.8. $C_{22}H_{38}IPSi_3$ requires C, 48.5, H, 7.0%). The *phosphonium salts* $[P\{CH(SiMe_3)_2\}Ph_2H]I$, yield 52%, m.p. 137—140 °C (Found: C, 48.0; H, 6.3. $C_{19}H_{30}IPSi_2$ requires C, 48.3; H, 6.4%), and $[P(CH_2SiMe_3)Ph_2H]I$, yield 68%, m.p. 167—169 °C (Found: C, 47.6; H, 5.6. $C_{16}H_{22}IPSi$ requires C, 48.0; H, 5.5%), were made similarly.

Methyldiphenyl[*tris*(*trimethylsilyl*)*methyl*]*phosphonium Iodide*.—Iodomethane (4 mmol) was added dropwise to $P[C(SiMe_3)_3]Ph_2$ (1.26 g, 3 mmol) in toluene (20 cm^3) and the mixture stirred overnight. White crystals of the *phosphonium salt* were filtered off and washed with toluene. Yield 82%, m.p. 154—156 °C (Found: C, 49.1; H, 7.1. $C_{23}H_{40}IPSi_3$ requires C, 49.5; H, 7.2%). The *compounds* $[P\{CH(SiMe_3)_2\}Ph_2Me]I$, yield 79% (Found: C, 49.3; H, 6.0. $C_{20}H_{32}IPSi_2$ requires C, 49.4; H, 6.6%), and $[P(CH_2SiMe_3)Ph_2Me]I$, yield 77%, m.p. >300 °C (Found: C, 49.4; H, 5.7. $C_{17}H_{24}IPSi$ requires C, 49.3; H, 5.8%), were made similarly. The [bis(trimethylsilyl)methyl]phosphonium salt was extremely hygroscopic.

[*Bis*(*trimethylsilyl*)*methylene*]*methyldiphenylphosphorane*.—When the phosphonium salt $[P\{C(SiMe_3)_3\}Ph_2Me]I$ was heated at 100 °C (0.3—0.5 Torr, *ca.* 40—67 Pa) in a small apparatus for distillation, iodotrimethylsilane, identified by its n.m.r. spectrum, was collected in the protecting cold trap, and the yellow liquid *ylid* $MePh_2P{=}C(SiMe_3)_2$ in the still receiver. Yield 50% (Found: C, 65.8; H, 8.6. $C_{20}H_{31}PSi_2$ requires C, 67.0; H, 8.6%). N.m.r. spectra: ^1H, δ 0.15 (s, Me_3Si), 2.13 [d, CH_3, $^2J(PCH)$ 12 Hz], and 7.4—8.0 (m, Ph); ^{31}P-{^1H}, δ 12.2.

Mass Spectra.—Significant peaks with relative abundances in parentheses, had *m*/*e* values as follows.

$P[C(SiMe_3)_3]Cl_2$: 332 (1, $[M]^+$), 224 {2, $[(Me_3Si)_2CPCl]^+$}, 209 {17, $[(Me_3Si)_2CPCl - Me]^+$}, 116 (22, $[Me_3SiCP]^+$), 101 (22, $[Me_3SiCP - Me]^+$), 93 (22), and 73 (100).

$P[C(SiMe_3)_3]H_2$: 264 (33, $[M]^+$), 249 (22, $[M - Me]^+$), 201 (7), 129 (16), and 73 (100).

$P[C(SiMe_3)_3]Ph_2$: 416 (27, $[M]^+$), 415 (9), 401 (6, $[M - Me]^+$), 343 (66), 185 (18), 183 (27), 135 (72), and 73 (100).

$P[CH(SiMe_3)_2]Ph_2$: 344 (18, $[M]^+$), 343 (18), 329 (7, $[M - Me]^+$), 253 (25), 196 (7), 186 (7), 185 (2), 183 (7), 145 (7), 135 (61), and 73 (100).

$(Me_3Si)_2C{=}PPh_2Me$: 358 (18, $[M]^+$), 357 (9, $[M - H]^+$), 343 (100, $[M - Me]^+$), 267 (14), 200 (10), 185 (18), and 183 (3).

$P(CH_2SiMe_3)Ph_2$: 272 (21, M^+), 271 (27, $[M - H]^+$), 257 (3, $[M - Me]^+$), 185 (6), 183 (4), 136 (7), 135 (55, $[SiPh_2Me]^+$), and 73 (100). Assignments were confirmed by accurate mass measurements.

Cleavage Studies.—The approximate compositions of mixtures of the various $P[C(SiMe_3)_nH_{3-n}]Ph_2$ species were determined by comparison of the heights of the relevant ^{31}P-{^1H} n.m.r. signals. In runs in the presence of acid, the mixtures had to be neutralized or made slightly basic with dilute methanolic NaOMe before the spectra were recorded. Unless otherwise indicated, the reactions were carried out under argon at room temperatures (*ca.* 21 °C), and details are as follows.

(*i*) A solution of $P[C(SiMe_3)_3]Ph_2$ (0.21 mmol) in MeOH (0.5 cm^3) was sealed under argon in an n.m.r. tube, and the ^{31}P-{^1H} n.m.r. spectra were recorded at appropriate intervals. The relative amounts of the species present at various times are shown in Table 2. The ^{13}C n.m.r. spectrum was recorded after 24 h and showed $SiMe_3(OMe)$ to be present.

(*ii*) In similar procedures but with (*a*) 0.05 mol dm^{-3} NaOMe–MeOH or (*b*) Bu^tOH as solvent, only unchanged $P[C(SiMe_3)_3]Ph_2$ was present after 7 d.

(*iii*) A solution of $P[C(SiMe_3)_3]Ph_2$ (0.22 g) in 0.05 mol dm^{-3} CF_3CO_2H in MeOH (1.5 cm^3) was made up in a Schlenk tube under argon. After 30 min half of the solution was removed and made slightly basic with NaOMe–MeOH, and its ^{31}P-{^1H} spectrum was recorded. This showed that only the $P[C(SiMe_3)_nH_{3-n}]Ph_2$ species with $n = 2$ and 1 were present, in 17 : 83 ratio. After 24 h the remainder of the reaction solution was similarly treated and shown to contain only the species with $n = 1$ and 0, in 74 : 26 ratio.

(*iv*) A solution of $[P\{C(SiMe_3)_3\}Ph_2H]I$ (0.05 mmol) in MeOH (0.6 cm^3) under argon was kept for 15 min then made slightly basic. The ^{31}P-{^1H} n.m.r. spectrum showed that the species $P[C(SiMe_3)_nH_{3-n}]Ph_2$ with $n = 2$, 1, and 0 were present in *ca.* 34 : 48 : 18 ratio.

(*v*) A solution of $[P\{C(SiMe_3)_3\}Ph_2Me]I$ (0.16 mmol) in MeOH (1 cm^3) was sealed under argon in an n.m.r. tube which was placed in the probe of the n.m.r. spectrometer (*ca.* 35 °C). After *ca.* 5 min, only $[P(CH_2SiMe_3)Ph_2Me]I$ and $[PPh_2Me_2]I$ were present, in *ca.* 27 : 73 ratio, and after 15 min only the latter species was detected.

(*vi*) A solution of $[P\{CH(SiMe_3)_2\}Ph_2Me]I$ (0.17 mmol) in 0.20 mol dm^{-3} NaOMe–MeOH (0.5 cm^3) under argon was examined after 30 min and found to contain only $[PPh_2Me_2]I$. The same result was obtained when a similar solution initially containing $[P(CH_2SiMe_3)Ph_2Me]I$ was kept for 13 min.

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