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New Silicon–Phosphorus Reagents in Organic Synthesis. Carbonyl and Conjugate Addition Reactions of Silicon Phosphite Esters and Related Systems

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Abstract: The 1,2- and 1,4-addition reactions of organosilicon tervalent phosphorus esters, X_2POSiR_3(X = OMe, NMe_2, Ph), with saturated and α,β-unsaturated aldehydes and ketones have been studied. These addition reactions have been compared with the complementary reactions of alkyl phosphorus esters, X_2POCH_3, and R_3SiCl with carbonyl substrates. With α,β-unsaturated aldehydes, a judicious choice of reagent and conditions leads to the regioselective 1,2- or 1,4-addition mode. Some of the mechanistic details of these addition reactions have been elucidated.

Introduction

Over the last 5 years the general utility of the reaction of organosilanes,[1] R_3SiX, with carbonyl substrates has been widely recognized (eq 1).[2-8] Possibly the central explanation

(1)

X = -CN,[2] $-N_3$,[3] -SR,[4] $-PR_2$,[5] $-C(N_2)CO_2Et$,[6] $-C{\equiv}CR$,[7] -H[8]

for the success in the development of such carbonyl insertion processes has been the recognition of specific modes of catalysis which facilitate such reactions.

In conjunction with our general interest in the development of synthetic operations which reverse the normal polar reactivity patterns of the carbonyl function, we have engaged in a general study of organosilane addition reactions to saturated and unsaturated aldehydes and ketones illustrated below (eq 2-4) where A is a potential carbanion-stabilizing function.[2a]

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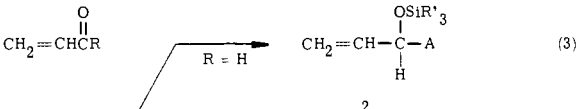

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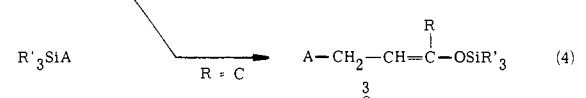
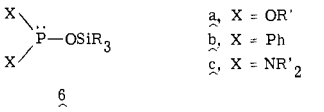


(4)

Upon strong-base metalation, adducts **1, 2,** and **3** should afford useful reversed polarity[9] equivalents such as carbonyl[2h,10] and homoenolate anions[11] **4** and **5**.

4 **5**

With the above objectives in mind we have undertaken a study of the 1,2- and 1,4-addition reactions of trialkylsilyl tervalent phosphorus esters **6**. The expected adducts derived



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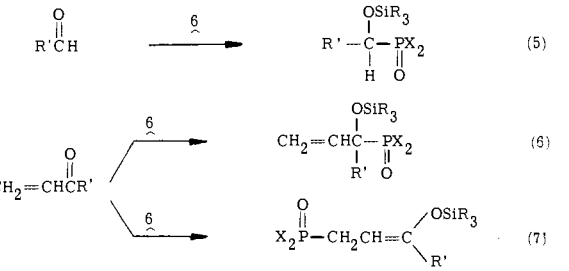
from **6** and aldehyde and ketone substrates are illustrated below (eq 5-7). In contrast to the alkyl tervalent phosphorus



(5)

(6)

(7)

esters **7**, X_2POY(Y = alkyl) which have been demonstrated to react with carbonyl derivatives by a manifold of reaction paths, it was anticipated the organosilicon esters **6** should undergo 1,2-addition with far greater facility based upon the mechanistic rationale presented in Scheme I. *In considering the addition of* **7** *(Y = SiR_3 or CR_3) to a carbonyl group, either a polar intermediate* **8** *or pericyclic transition state* **9** *is reasonable for Y = SiR_3 but not for Y = CR_3.* This prediction is based upon the fact that intramolecular migration of silicon via front-side displacement with retention of configuration is well documented.[12] In contrast, the analogous stepwise or concerted *intramolecular* alkyl transfer process (cf. **8** or **9**, Y = CR_3) is strongly disfavored.[13] In fact, when aliphatic aldehydes are heated in the presence of trialkyl phosphites, only a maximum of 24% of the carbonyl insertion product has been reported,[14] and these adducts have been suggested to be derived from *intermolecular* alkyl transfer.[15] Similar arguments *may* also apply to 1,4-addition reactions of X_2P–OY (Y = silicon vs. carbon) with unsaturated carbonyl substrates. It may thus be assumed that the carbonyl addition process of silyl phosphorus esters **6** might proceed by well-defined reaction paths

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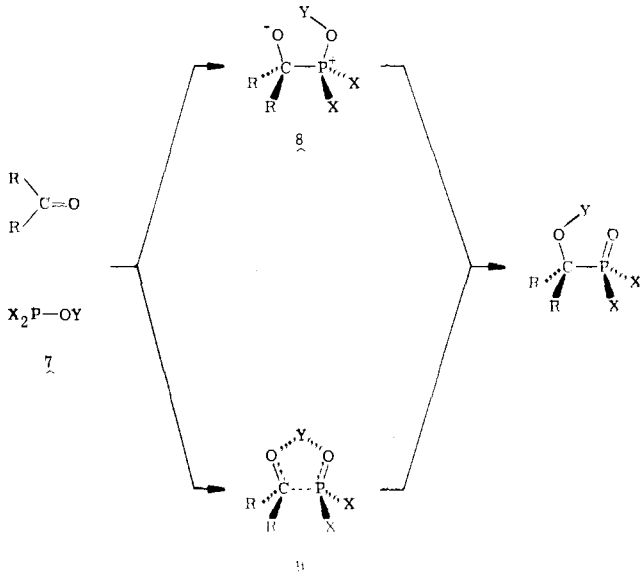
Table I. Tervalent Phosphorus-Silicon Reagents, X_2POSiR_3, **6**

X_2POSiR_3	Method of synthesis[a]	Yield, %[b]	Ref
$(MeO)_2POSiMe_3$, **10**	I	*c,c*	17,18
$(MeO)_2POSiEt_3$, **11**	I	*c*	17
$(EtO)_2POSiMe_3$, **12**	I	55	19[d]
	II	53	19
$(EtO)_2POSiEt_3$, **13**	I	53, 62	19,20
	II	58	9
$Ph_2POSiMe_3$, **14**	I	55, 81	21
$(Et_2N)_2POSiMe_3$, **15**	I	35	22

[a] General method of synthesis: method I, $X_2PO^- + R_3SiCl$; method II, $X_2PCl + R_3SiO^-$. [b] Yields are for distilled material. [c] Yield was not reported. [d] From $(EtO)_2PONa + Me_3SiBr$.

Scheme I



in contrast to the spurious behavior observed with alkyl phosphites.

Reagents

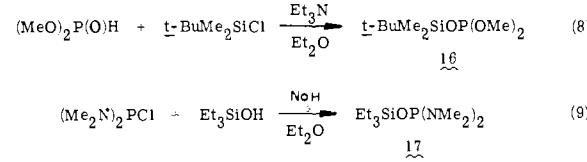
At the outset, a number of tervalent phosphorus-silicon reagents had been reported,[16] and subsequently others have been synthesized during the course of this project. Those that presented the greatest potential for this work are listed in Table I.

Two general methods of synthesis are available for the preparation of X_2POSiR_3. The first (method I) proceeds via the deprotonation of $X_2P(O)H$ either completely with a strong base (NaH) or with trialkylamines. The conjugate base is subsequently O-silylated with a trialkylchlorosilane. The alternate procedure (method II) involves the treatment of X_2PCl with the conjugate base of a trialkylsilanol. Although the two approaches are complementary in nature, the first approach (method I) is generally the more useful based upon the wide availability of various trialkylchlorosilanes and phosphinylidene reagents.

Four silicon-phosphorus reagents were prepared for examination for insertion reactions in carbonyl substrates. Dimethyl trimethylsilyl phosphite[17] (**10**) and dimethyl triethylsilyl phosphite[17] (**11**) were prepared by a variation of known procedures.[19,20] Dimethyl *tert*-butyldimethylsilyl phosphite (**16**) was prepared analogously from dimethyl phosphite and *tert*-butyldimethylchlorosilane. Triethylsilyl *N,N,N′,N′*-tetramethyl phosphorodiamidite (**17**) was prepared from *N,N,N′,N′*-tetramethyl phosphonodiamidochloride[23] and triethylsilanol.[24] All four reagents are clear, mobile liquids

Table II. Addition Reactions of X_2POSiR_3 to Saturated Carbonyl Substrates (eq 10)

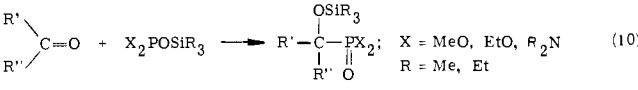
Carbonyl Substrate	X_2POSiR_3	% Yield	Reference
C_6H_5CHO	$(EtO)_2POSiMe_3$, 12	80	25
CH_3CHO	12	70	25
$C_2H_5COCH_3$	12	55	25
	12	52	25
$CH_3COCH_2CO_2C_2H_5$	12	62	25
$C_6H_5COCH_3$	$(MeO)_2POSiEt_3$, 11	27	17
$CH_3COP(O)(OEt)_2$	12	62	30
CCl_3CHO	12	92	28
CF_3COCF_3	12	95	29
$CH_3COCO_2CH_3$	12	36	31
C_6H_5CHO	$(Et_2N)_2POSiMe_3$, 15	71	27



which are readily hydrolyzed by traces of moisture and oxidized by air.

Reactions of X_2POSiR_3 with Saturated Aldehydes and Ketones

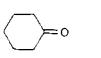
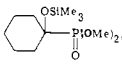
During the development of this project, Pudovik and others in a series of brief reports described the reaction of several tervalent silicon-phosphorus reagents with a variety of carbonyl substrates. These workers observed that dialkyl trialkysilyl phosphites and trialkylsilyl tetramethylphosphorodiamidites react smoothly with saturated aldehydes and ketones to produce α-siloxyphosphonates and α-siloxyphosphonamides (eq 10). The carbonyl substrates included saturated aldehydes



and ketones,[17,25] aromatic aldehydes[17,25-27] and ketones,[17] chloral,[28] hexafluoroacetone,[29] and acyl phosphonates,[30] esters,[31] and nitriles.[31] Representative cases are contained in Table II.

Concurrent with the appearance of the work of Pudovik, investigations in our laboratory have confirmed and extended these observations. The results of the present study are summarized in Table III. For the cases summarized, 1 equiv each of aldehyde or ketone and silicon-phosphorus reagent were combined either neat or in solution (C_6H_6 or Et_2O) under an inert atmosphere. The reaction progress was monitored by ^1H NMR in all instances. The reaction times and temperatures can be qualitatively employed to gauge the "relative reactivities" of the individual phosphorus reagents with the indicated carbonyl substrate. For the cases reported, the carbonyl addition reactions are characteristically efficient and generally devoid of side reactions such as enol silylation. In most instances the yields determined by ^1H NMR analysis were nearly quantitative. As expected, for a given phosphorus reagent, the following order of reactivity was observed: RCHO > ArCHO > RCOR (cf. Table III). The effects of increased steric congestion about silicon in the tervalent phosphorus reagent, X_2POSiR_3, are apparent. A qualitative comparison of the relative reactivities of 1-hexanal with both **10** and **16** (entries

Table III. Addition Reactions of X_2POSiR_3 to Saturated Carbonyl Substrates (eq 10)

Entry	Carbonyl Substrate	X_2POSiR_3	Adduct	Conditions	% Yield Isolated
1	$i\text{-}C_3H_7CHO$	$(MeO)_2POSiMe_3$, **10**	$i\text{-}C_3H_7\text{-}CH(OSiMe_3)\text{-}P(O)(OMe)_2$, **18**	25°C, 1 h[a]	82
2	$n\text{-}C_5H_{11}CHO$	**10**	$n\text{-}C_5H_{11}\text{-}CH(OSiMe_3)\text{-}P(O)(OMe)_2$, **19**	25°C, 1 h[b]	81
3	C_6H_5CHO	**10**	$C_6H_5\text{-}CH(OSiMe_3)\text{-}P(O)(OMe)_2$, **20**	25°C, 24 h[b]	97
4	CH_3COCH_3	**10**	$CH_3\text{-}C(CH_3)(OSiMe_3)\text{-}P(O)(OMe)_2$, **21**	90°C, 24 h[a]	74
5	$n\text{-}C_5H_{11}COCH_3$	**10**	$n\text{-}C_5H_{11}\text{-}C(CH_3)(OSiMe_3)\text{-}P(O)(OMe)_2$, **22**	95°C, 36 h[a]	62
6		**10**	 **23**	95°C, 13 h[a]	86
7	$n\text{-}C_5H_{11}CHO$	$(MeO)_2POSiMe_2t\text{-}Bu$, **16**	$n\text{-}C_5H_{11}\text{-}CH(OSiMe_2t\text{-}Bu)\text{-}P(O)(OMe)_2$, **24**	100°C, 3 h[a]	81
8	C_6H_5CHO	**16**	$C_6H_5\text{-}CH(OSiMe_2t\text{-}Bu)\text{-}P(O)(OMe)_2$, **25**	25°C, 6 h[a]	65
9	$C_6H_5COCH_3$	**16**	$C_6H_5\text{-}C(CH_3)(OSiMe_2t\text{-}Bu)\text{-}P(O)(OMe)_2$, **26**	120°C, 48 h[a]	34
10	C_6H_5CHO	$(Me_2N)_2POSiEt_3$, **17**	$C_6H_5\text{-}CH(OSiEt_3)\text{-}P(O)(NMe_2)_2$, **27**	0°C, 0.5 h[c]	92
11	$n\text{-}C_6H_{13}CHO$	**17**	$n\text{-}C_6H_{13}\text{-}CH(OSiEt_3)\text{-}P(O)(NMe_2)_2$, **28**	0°C, 0.5 h[c]	97
12	CH_3CHO	**17**	$CH_3\text{-}CH(OSiEt_3)\text{-}P(O)(NMe_2)_2$, **29**	0°, 0.5 h[c]	83

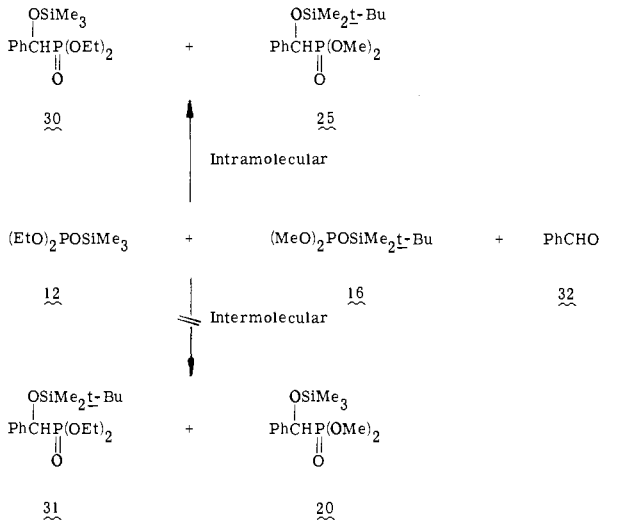
[a] Reaction carried out without solvent. [b] Reaction solvent: C_6H_6. [c] Reaction solvent: Et_2O.

2, 7) confirms that increased steric hindrance on silicon retards the rate of carbonyl addition. This rate retardation is undoubtedly associated with slower rates of silicon transfer in the addition process (Scheme I).

The relative reactivity of the phosphorus reagent X_2POSiR_3 as a function of X is firmly established. A comparison of **17** with the other reagents, **10** and **16,** clearly reveals that amine ligands on phosphorus dramatically increase the rate of carbonyl addition. A similar rate correlation has been reported for the reaction of tervalent phosphorus reagents with methyl iodide: $(MeO)_3P$, $k_{rel} = 1.00$; $(Me_2N)_3P$, $k_{rel} = 2250$ in S_N2 substitution reactions.[32]

Although it has been assumed that the carbonyl insertion reactions of trialkylsilyl phosphite esters proceed via *intramolecular* silicon transfer, no relevant experiments have been reported which confirm this point. Accordingly, the following crossover experiment was carried out (Scheme II). Equimolar amounts of $Me_3SiOP(OEt)_2$ (**12**) and $t\text{-}BuMe_2SiOP(OMe)_2$ (**16**) were allowed to react with 2 equiv of benzaldehyde. If the reaction proceeds via an intramolecular mechanism, adducts **30** and **25** would be the exclusive products. On the other hand, if intermolecular silicon transfer were occurring, adducts **31** and **20** would also be present in the product mixture. Careful analysis of the reaction mixture by NMR and gas chromatography indicated that *only* adducts **30** and **25** were formed. An independently synthesized sample of the crossover adduct **20** (Table III, entry 3) was definitively shown to be absent from the reaction mixture (≤2%) by gas chromatographic analysis. *It is thus concluded that the addition of the silyl phosphite ester* **12** *and* **16** *to aldehydes involves exclusive intramolecular silicon transfer.*

Scheme II



Some time ago a new reaction of demonstrated generality was reported by Birum in the patent literature.[33] This patent claims that α-silyloxy phosphonate esters can be readily prepared from either aldehydes or ketones, chlorosilanes, and trialkyl phosphite esters. A representative reaction and conditions are illustrated below (eq 11). This reaction is relevant

$$CH_3CH + Me_3SiCl + (MeO)_3P \xrightarrow[1/2\ h]{35\text{-}80°C} CH_3CH(OSiMe_3)P(O)(OMe)_2 \quad 97\% \quad (11)$$

33

to the present study in that mixed silyl phosphite esters (cf. **10**) could be produced in situ by an Arbuzov rearrangement, a reaction which has literature precedent (eq 12).[34] A control

$$(MeO)_3P + Me_3SiCl \xrightarrow[?]{\Delta} (MeO)_2POSiMe_3 + MeCl \quad (12)$$

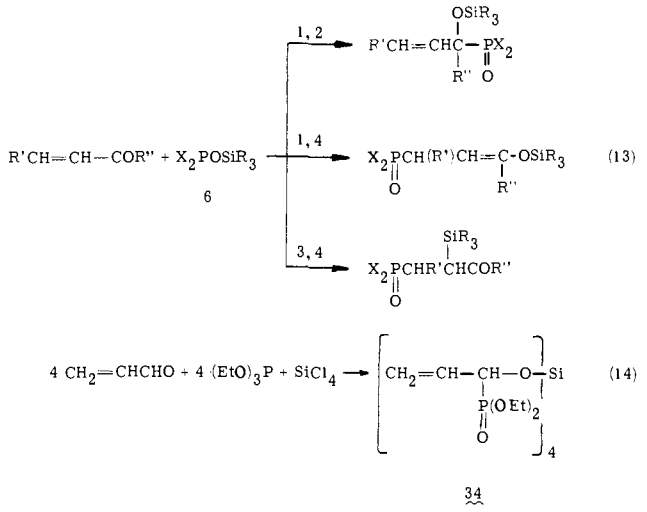
10

experiment, however, clearly demonstrates that **10** is *not* an intermediate in the above reaction reported by Birum.[33] Upon heating an equimolar mixture of trimethyl phosphite and chlorotrimethylsilane for 7 h at 105 °C, there was no evidence (^1H NMR) of the formation of the silyl phosphite **10** or any other reaction product. Since this control experiment was carried out at higher temperatures and longer reaction times (7 h, 105 °C vs. 35–80 °C, 0.5 h) than the case reported by Birum, one could speculate that adduct **33** might be formed in accordance with the mechanism outlined in Scheme III (vide supra).

Operationally, α-silyloxy phosphonate esters are readily obtained in high yields via the bimolecular addition of mixed silyl phosphite esters to carbonyl substrates (eq 10) or via the termolecular process reported by Birum (eq 11).[33] From the standpoint of simplicity, the latter reaction may be the method of choice, although this point has not been documented in the present study.

Reactions of X_2POSiR_3 with α,β-Unsaturated Aldehydes and Ketones

There exist three cases in the literature which document the reaction of mixed silyl phosphorus reagents, X_2POSiR_3, with α,β-unsaturated carbonyl derivatives.[25,35] In the cases studied, mixtures of adducts resulting from 1,2, 1,4, and 3,4 modes of addition have been reported (eq 13). These reports did not provide details on product ratios or adduct stereochemistry (in the case of 1,4-addition). In the only related study, the previously discussed two-reagent procedure described by Birum[33] has been applied to acrolein (eq 14). It was reported that the



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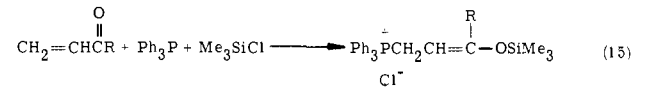
1,2 adduct **34** was obtained in unspecified yield. As a consequence of our interest in developing these reactions into preparatively useful processes, we have undertaken a detailed study of the addition reactions of X_2POSiR_3 (**6**) (method A) and X_2POR', R_3SiCl (method B) to α,β-unsaturated ketones and aldehydes.[36]

The reactions of the mixed silicon-phosphorus reagents **6** (method A) with a series of α,β-unsaturated aldehydes and ketones were carried out with 1 equiv of each reagent either neat or in solvent under an inert atmosphere. The aldehyde addition reactions generally proceeded at a convenient rate at ambient temperatures while ketonic substrates required heating. The complementary procedure employing the phosphorus esters, X_2POR, and trialkylchlorosilanes (method B) was carried out with stoichiometric quantities of each reagent in sealed ampules.

An additional reaction which we have briefly investigated for the introduction of phosphorus activating functions into enone substrates is illustrated below (eq 15). Conceptually, this



reaction is related to the reaction reported by Birum (eq 14), although this approach to the synthesis of enol phosphonium salts has heretofore been unreported. These reactions are conveniently carried out in anhydrous benzene at room temperature with equimolar quantities of phosphine, chlorosilane, and enone. After a brief induction period, the enol phosphonium salts separate from solution either as a salt or viscous oil (Table IV, entries 5, 6, 17). These salts were readily identified by their characteristic spectroscopic properties; however, their extreme lability toward hydrolysis precluded combustion analysis, and their instantaneous fragmentation under mass spectral conditions did not permit elemental composition to be determined. The scope of this reaction seems limited as substitution at the β position of the enone system precludes the formation of the phosphonium salt. This facet was demonstrated by a lack of reactivity with crotonaldehyde, cinnamaldehyde, and cyclohexenone.

The results summarized in Table IV reveal a number of useful observations relating those reaction parameters which exercise regiochemical control in these addition reactions. A comparison of silyl phosphite **10** (method A) with the two-reagent alternative (method B) in addition reactions with acrolein (Table IV, entries 1, 2) reveals that the former reagent system affords nearly a 1:1-mixture of 1,2 and 1,4 adducts while the latter gives *only* the 1,2-addition product **35**. The same trend in regioselectivity was observed with crotonaldehyde (entries 7, 8). The relative reactivities of the silyl phosphite and silyl phosphordiamidite reagents **10** and **17** parallel our earlier observations (Table III).

Table IV. Addition Reactions of Mixed Silicon-Phosphorus Reagents with Unsaturated Carbonyl Substrates (eq 13)

Entry	Substrate	Method[a]	Conditions[b]	Adducts[c]	% Yield[d]
1	CH_2=CHCHO	$(MeO)_2POSiMe_3$ (A) **10**	25 °C, 12 h	CH_2=CHCH(OSiMe$_3$)P(O)$(OMe)_2$, **35** (47%); $(MeO)_2P(O)CH_2CH$=CHOSiMe$_3$, **36** (53%)	86
2	CH_2=CHCHO	$(MeO)_3P$, Me_3SiCl (B)	25 °C, 4 h	**35**	70
3	CH_2=CHCHO	$(Me_2N)_2POSiEt_3$ (A) **17**	0 °C, 0.25 h[e]	CH_2=CHCH(OSiEt$_3$)P(O)$(NMe_2)_2$, **37**	90
4	CH_2=CHCHO	Ph_2POMe, Et_3SiCl (B)	100 °C, 0.5 h	$Ph_2P(O)CH_2CH$=CHOSiEt$_3$, **38**	(100)
5	CH_2=CHCHO	Ph_3P, Me_3SiCl (B)	25 °C, 0.25 h[f]	$Ph_3\overset{+}{P}CH_2CH$=CHOSiMe$_3$ Cl^-, **39**	(100)
6	CH_2=C(CH$_3$)CHO	Ph_3P, Me_3SiCl (B)	25 °C, 2 h[f]	$Ph_3\overset{+}{P}CH_2C(CH_3)$=CHOSiMe$_3$ Cl^-, **40**	(100)
7	CH_3CH=CHCHO	$(MeO)_2POSiMe_3$ (A) **10**	55 °C, 18 h	CH_3CH=CHCH(OSiMe$_3$)P(O)$(OMe)_2$, **41** (75%); $(MeO)_2P(O)CH(CH_3)CH$=CHOSiMe$_3$, **42** (25%)	91
8	CH_3CH=CHCHO	$(MeO)_3P$, Me_3SiCl (B)	55 °C, 3 h	**41**	92
9	CH_3CH=CHCHO	$(Me_2N)_2POSiEt_3$ (A)[e] **17**	0 °C, 0.5 h	CH_3CH=CHCH(OSiEt$_3$)P(O)$(NMe_2)_2$, **43**	95
10	PhCH=CHCHO	$(Me_2N)_2POSiEt_3$ (A)[e] **17**	0 °C, 0.5 h	PhCH=CHCH(OSiEt$_3$)P(O)$(NMe_2)_2$, **44**	93
11	CH_2=CHCOCH$_3$	$(MeO)_2POSiMe_3$ (A) **10**	50 °C, 6 h	$(MeO)_2P(O)CH_2CH(OSiMe_3)CCH_3$, **45**	88
12	CH_2=CHCOCH$_3$	$(MeO)_3P$, Me_3SiCl (B)	100 °C, 2 h	**45**	79
13	CH_2=CHCOCH$_3$	$(MeO)_2POSiEt_3$ (A) **11**	100 °C, 3 h	$(MeO)_2P(O)CH_2CH(OSiEt_3)CCH_3$, **46**	36
14	CH_2=CHCOCH$_3$	$(MeO)_3P$, Et_3SiCl (B)	100 °C, 2 h	**46**	76
15	CH_2=CHCOCH$_3$	$(Me_2N)_2POSiEt_3$ (A)[e] **17**	0 °C, 0.5 h	$(Me_2N)_2P(O)CH_2CH$=CCH_3, **47**	82
16	CH_2=CHCOCH$_3$	Ph_2POMe, Et_3SiCl (B)	100 °C, 0.5 h	$Ph_2P(O)CH_2CH$=CCH_3, **48**	(100)
17	CH_2=CHCOCH$_3$	Ph_3P, Me_3SiCl (B)[g]	25 °C, 0.25 h	$Ph_3\overset{+}{P}CH_2CH$=CCH_3 Cl^-, **49**	(100)
18	CH_3CH=CHCOCH$_3$	$(MeO)_2POSiMe_3$ (A)	80 °C, 24 h	$(MeO)_2P(O)CH(CH_3)CH$=CCl_3, **50**	84

[a] Method A, X_2POSiR_3 + enone; Method B, X_3SiCl + enone. [b] Except where noted the reactions were carried out in the absence of solvent. [c] Product ratios in parentheses. [d] Yields reported are of distilled products. Yields in parentheses were determined by NMR experiments; in such cases attempts at purification resulted in decomposition. [e] The reaction was carried out 3M in THF. [f] The reaction was carried out 3M in benzene.

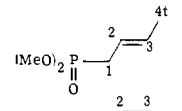
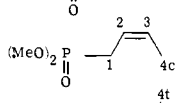
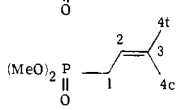
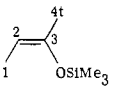
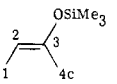
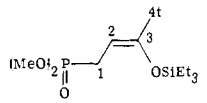
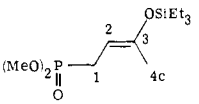
Whereas **10** reacted slowly with acrolein (neat) over a 12-h period at 25 °C (entry 1), **17** added exothermically at 0 °C to a range of α,β-unsaturated aldehydes exclusively via the 1,2-addition mode (entries 3, 9, 10). On the other hand, methyl vinyl ketone underwent uniform 1,4-addition with both **10** and **17**, as well as the two-reagent phosphite-chlorosilane system (method B).

An examination of the olefin geometries of the 1,4-addition products in Table IV reveals a pattern of stereochemical control. With the exception of adducts **36** and **42**, which were shown to be mixtures of *E* and *Z* isomers (entries 1, 7), the other 1,4 adducts of both aldehydes (entries 4, 5) and methyl vinyl ketone (entries 11-18) possessed exclusively the *Z*-olefin geometry (vide infra).

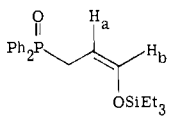
Stereochemical Assignments of 1,4 Adducts

As a consequence of possible mechanistic implications, a rigorous assignment of olefin geometry was undertaken for the 1,4 adducts listed in Table IV. The assignment of the olefin geometries of the acrolein adducts **38** and **39** were conveniently made by ^1H NMR spectroscopy. The observed vicinal olefinic coupling constants, J_{ab}, of 6.0 Hz for both **38** and **39** agree

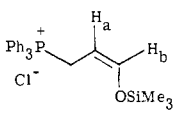
Table V. ^{13}C NMR Chemical Shifts[a] of **46Z**, **46E**, and Related Compounds

Compound	C_1	C_2	C_3	C_{4t}	C_{4c}
	29.6	120.2	130.4	17.9	
	24.8[b]	119.2	128.5		12.7
	26.0[c]	113.3	137.2	25.8	18.0
	10.8[d]	102.6	147.6	22.6	
	12.0[d]	101.2	148.6		17.4
	21.5[c]	95.3		21.4	
	23.2[d]	97.1	149.8	22.5	
	23.7[c]	95.3			16.8
	24.9[d]	96.5	151.6		17.9

[a] δ ^{13}C parts per million downfield from Me_4Si. [b] Spectrum taken of neat compound. [c] Spectrum taken in $CDCl_3$. [d] Spectrum taken in C_6D_6.



38

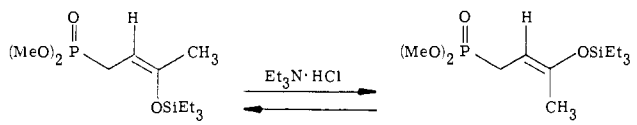


J_{ab} = 6.0 Hz

39

closely with the reported vicinal olefinic coupling constant of 6.1 Hz for *cis*-1-trimethylsilyloxy-1-butene.[37] In contrast, the *trans*-butene isomer exhibits a corresponding coupling constant of 12.1 Hz.

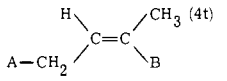
An unambiguous assignment of the trisubstituted olefin geometries to the methyl vinyl ketone adducts **45–50** required the preparation of both the *E* and *Z* olefin isomers. Acid-catalyzed equilibration of phosphonate **46** (Et_3N·HCl, 120 °C, 6 h) afforded a 1.7:1 ratio of **46Z** and **46E**, respectively (vide



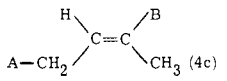
46Z 46E

infra) along with ca. 5% of the terminal vinyl ether, RC(OSiEt$_3$)=CH$_2$. A tentative stereochemical assignment of the olefin geometries can be made by comparing the ^1H NMR chemical shifts of the vinylic protons in **46Z** (4.53 ppm) and **46E** (4.80 ppm) in C_6D_6. The chemical shift difference, $\Delta\delta$, of 0.27 ppm is close to that reported for the *Z* (4.51 ppm) and *E* isomer (4.73 ppm) 2-trimethylsilyloxy-2-butene.[37] House and others have made the generalization that olefin isomers with the β-vinyl hydrogen and oxygen functions cis (e.g., **46E**) exhibit the vinyl proton resonance at a lower field (0.1–0.3 ppm) that the corresponding trans isomers.[37,38] This correlation appears to hold for isomers **46Z** and **46E**.

A more convincing structural assignment was made through a comparison of the ^{13}C NMR chemical shifts of **46Z** and **46E** with the structurally related olefins shown in Table V. The salient data in this table may be summarized with structures I and II below. It is generally accepted that cisoid olefinic



I



II

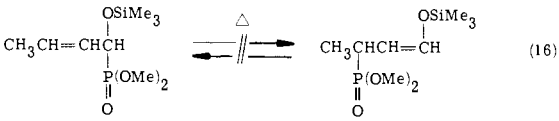
Variables	$\Delta\delta(C_{4t} - C_{4c})$ ppm	Solvent
A = H; B = CH_3	+8.4[40a]	CS_2
A = H; B = $OSiMe_3$	+5.2	$CDCl_3$
A = P(O)(OMe)$_2$; B = H	+5.2	neat
A = P(O)(OMe)$_2$; B = CH_3	+7.8	$CDCl_3$
A = P(O)(OMe)$_2$; B = $OSiEt_3$	+4.6	$CDCl_3$, C_6D_6

carbons (cf. II, C_{4c}) are shielded relative to the isomeric transoid olefinic carbons (cf. I, C_{4t}); such shielding has been attributed to both electronic and steric effects.[39,40] As illustrated in I and II, the chemical shift difference, $\Delta\delta$, between the transoid and cisoid olefinic methyl groups correlates exceptionally well for a range of relevant subtituents A and B. Consequently **46Z** and **46e** must possess the indicated olefin geometries. Adducts **45, 47, 48, 49,** and **50** were each assigned the *Z*-olefin geometry based upon the aforegoing logic.

Mechanistic Considerations

An all-encompassing mechanistic rationale which correlates the data presented in Tables III and IV is beyond the scope of the present study. However, several experimental probes have been applied to provide some insight into the nature of the reactions of the tervalent phosphorous reagents employed in this investigation with α,β-unsaturated carbonyl substrates.

The possibility that the 1,2 and 1,4 adducts were thermally interconvertible was eliminated by the following study. The crotonaldehyde adducts **41** and **42** were individually heated at temperatures up to 200 °C in an attempt to equilibrate the addition products (eq 16). No interconversion was detected.



(16)

41 42

The high thermal stability observed in this instance suggests that the 1,2-:1,4-adduct ratios reported in Table IV are a consequence of kinetic control during the addition process and are not the result of a thermal equilibration.

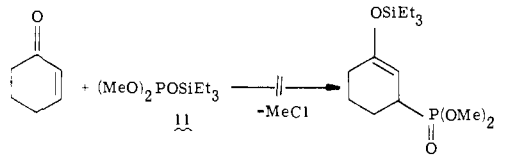
In order to determine whether solvent dielectric might play a significant role in altering the relative rates of 1,2- vs. 1,4-addition, the reaction of dimethyl trimethylsilyl phosphite (**10**) with both acrolein and crotonaldehyde (cf. Table IV, entries 1, 7) in a range of solvents was undertaken (Table VI). Although there was an observed ninefold increase in total rate of product formation in comparing *n*-hexane and dimethyl sulfoxide as solvents, there was only a minor alteration in the 1,2-:1,4-adduct ratio (ca 1:1 in Me_2SO and 2:1 in *n*-C_6H_{14}). The small solvent dependence on the rates of both 1,2- and 1,4-addition strongly suggests that the rate-determining steps in *both* processes involve transition states possessing little charge separation.[41]

The observation of *Z*-olefin geometry in many of the 1,4 adducts (Table IV) suggests that a cisoid enone geometry might be either obligatory or highly preferred for 1,4-addition. In this regard it is noteworthy that cyclohexenone fails to react with either silyl phosphite **11** (105 °C, 52 h) or with equimolar

Table VI. Solvent Effects in the Addition of Dimethyl Trimethylsilyl Phosphite (10) to Unsaturated Aldehydes

Aldehyde	Solvent	ϵ^a	$T_{1/2}$,[b] h	1,2 adduct	1,4 adduct[c,d]	Yield, %[e]
CH_2=CHCHO	None			47	53	88
CH_2=CHCHO	Me_2SO	46.7	1	47	53	*f*
CH_2=CHCHO	C_6H_6	2.27	6.7	57	43	85
CH_2=CHCHO	C_6H_{14}	1.88	9	67	33	77
CH_3CH=CHCHO	None			75	25	90
CH_3CH=CHCHO	Me_2SO	46.7	17	68	32	*f*
CH_3CH=CHCHO	C_6H_6	2.27	56	88	12	*f*

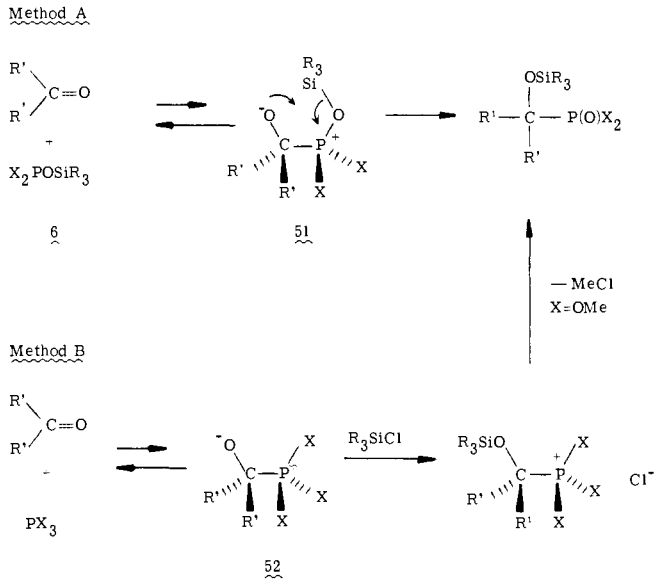
[a] Dielectric constant of reaction solvent at 25 °C. [b] Approximate times for the reaction to proceed to 50% completion at 1 M concentration for reactants. [c] Ratios determined by NMR integration. [d] 1,4 adducts are mixtures of *E* and *Z* isomers. [e] Distilled yields. [f] NMR experiment; yield not obtained.



quantities of trimethyl phosphite and chlorotriethylsilane (55 °C, 28 h).

A permissive general mechanistic account of the 1,2-addition reactions of the silyl phosphorus reagents X_2POSiR_3, X = OR′, NMe_2, Ph (method A), as well as the two-reagent system reported by Birum[33] (method B) is summarized in Scheme III. We have demonstrated that *intramolecular* silicon

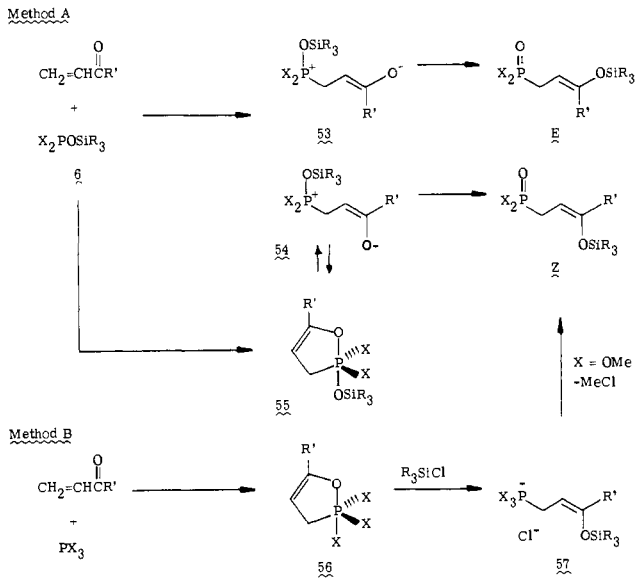
Scheme III



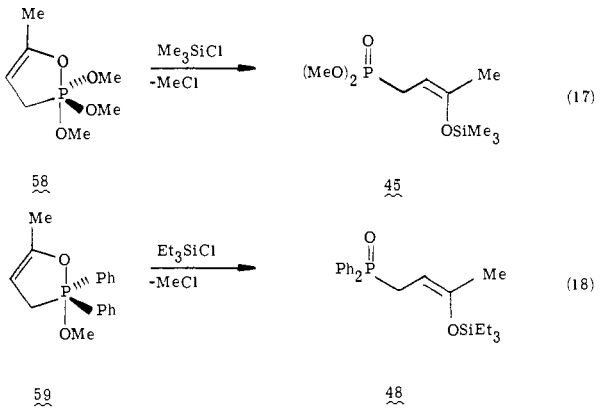
transfer from **51** is required. Furthermore, dipolar adducts **51** and **52** are reasonable intermediates. The isolation of a related 1:1 adduct **52** (X = NMe_2) between benzaldehyde and hexamethylphosphorous triamide supports this postulate.[42]

A general accounting of the observations associated with 1,4-addition are illustrated in Scheme IV. The preferential formation of *Z* adducts as well as the unreactivity of transoid enones suggests a propensity for the formation of the *Z* enolate **54**, possibly via oxaphospholenes **55** or **56**. The preparation of oxaphospholenes by the addition of tervalent phosphorus derivatives to enones is well documented.[43] Supporting evidence for the inclusion of oxaphospholenes in this reaction scheme came from the synthesis and subsequent silylation of **58**[43a] and **59**. Treatment of **58** and **59** with chlorotrimethylsilane and chlorotriethylsilane, respectively (0 °C, 5 min), resulted in an exothermic reaction accompanied by the formation of methyl chloride and the *Z* adducts **45** and **48** in ≥95% yield (eq 17, 18).

Scheme IV



At the present time a complete understanding of those reaction parameters which influence the relative rates of 1,2- and 1,4-addition of tervalent phosphorus reagents to enone systems



is lacking. However, from an operational standpoint, a judicious choice of reagent systems results in the regioselective addition of phosphorus activating groups to unsaturated carbonyl substrates.

Projections

A wealth of invaluable synthetic transformations employing phosphorus-stabilized carbanions has evolved over the last 2 decades.[44] The objectives of this current study have been aimed at the exploration of new techniques of readily incorporating phosphorus activating groups into carbonyl-containing organic substrates. The subsequent synthetic utility of the organophosphorus reagents prepared during the course of this study will be reported shortly.

Experimental Section

Diethyl ether, benzene, THF, and hexane were dried by distillation under nitrogen from lithium aluminum hydride or benzophenone ketyl. Triethylamine was distilled under nitrogen from calcium hydride. Trimethylchlorosilane and triethylchlorosilane[24] were distilled under nitrogen from calcium hydride, the distillate treated with triethylamine, and the triethylamine hydrochloride removed by centrifugation prior to use. Aldehydes and ketones were freshly distilled.

Unless otherwise specified, all reactions were carried out under an atmosphere of nitrogen with the rigid exclusion of moisture from reagents and glassware.

Infrared spectra were recorded on a Perkin-Elmer Model 700 or a Beckman 4210 spectrophotometer. Proton nuclear magnetic resonance spectra were recorded on a Varian Associates Model T-60 or A-60 spectrometer. Chemical shifts are reported in parts per million on the δ scale relative to a tetramethylsilane internal standard or chloroform or benzene for silicon-containing compounds. In NMR descriptions, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and J_D = signal splitting due to diastereotopic nonequivalence. Carbon-13 nuclear magnetic resonance spectra were recorded on a Varian Associates XL-100 or a Varian Associates Model T-60 equipped with a Nicolet TT-7 pulsed Fourier transform system. Chemical shifts are reported in parts per million on the δ scale relative to tetramethylsilane internal standard or $CDCl_3$ (76.9 ppm) or C_6D_6 (128.0 ppm) for silicon-containing compounds.

Analytical gas chromatographic analyses were performed on a Varian Aerograph Model 1440 gas chromatograph using 2-m columns of 5% SE-30, 5% SE-52, 5% FFAP, or 5% Carbowax 20M on a 60–80 mesh DMCS Chromosorb W support. Preparative gas chromatographic separations were performed on a Varian Aerograph Model 90-P instrument using a 2-m column of 15% SE-30 on 40–60 mesh Chromosorb W support.

Mass spectra were recorded on an AEI MS-9 or a Du Pont MS 21-491 mass spectrometer by Ms. Elizabeth Irwin, Department of Chemistry, University of California, Los Angeles, or on a Du Pont MS 21-492 B mass spectrometer by Dr. Susan Rottschaefer, Division of Chemistry and Chemical Engineering, California Institute of Technology.

Microanalyses were performed by Miss Heather King, Department of Chemistry, University of California, Los Angeles, Dr. Susan Rottschaeffer, Division of Chemistry and Chemical Engineering, California Institute of Technology, or Spang Microanalytical Laboratory, Ann Arbor, Mich.

Dimethyl Trimethylsilyl Phosphite (10). The title compound was prepared from dimethyl phosphite and trimethylchlorosilane in benzene–triethylamine as described by Nesterov[17] in 59% yield, bp 73–75 °C (56 mm).

Dimethyl Triethylsilyl Phosphite (11). The title compound was prepared from dimethyl phosphite and triethylchlorosilane in benzene–triethylamine as described by Nesterov[17] in 59% yield, bp 83 °C (10 mm).

Diethyl Trimethylsilyl Phosphite (12). The title compound was prepared from diethyl phosphite and trimethylchlorosilane in diethyl ether–triethylamine as described by Bugerenko[19] in 72% yield, bp 63–65 °C (15 mm).

Dimethyl *tert*-Butyldimethylsilyl Phosphite (16). To a flask, equipped with a reflux condenser, a mechanical stirrer, and an addition funnel, were added 500 mL of anhydrous THF and 7.57 g (0.315 mmol) of sodium hydride in a mineral oil dispersion. While the reaction flask was cooled in an ice bath, 25.7 mL (30.8 g, 0.28 mol) of dimethyl phosphite was added dropwise. Upon completion of addition, the solution was refluxed for 2.5 h. Upon cooling to room temperature, 39.2 g (0.26 mmol) of *tert*-butyldimethylchlorosilane was added in one portion. The reaction mixture was refluxed for 18 h and filtered. Distillation at atmospheric pressure removed the solvent. Subsequent vacuum distillation afforded 27.0 g (46%) of silyl phosphite **16:** bp 85–90 °C (16 mm); IR (neat) 1255 ($SiMe_3$), 1060 (Si–O) and 1030 cm^{-1} [$P(OMe)_2$]; NMR ($CDCl_3$) δ 3.42 [d, 6, J_{PH} = 10 Hz, $P(OMe)_2$], 0.92 (s, 9, *t*-BuSi), and 0.17 ppm (s, 6, $SiMe_3$).

Exact mass (75 eV) *m/e* calcd for $C_8H_{21}O_3PSi$: 224.100. Found: 224.097.

Triethylsilyl *N,N,N′,N′*-Tetramethyl Phosphorodiamidite (17). To a three-necked flask, equipped with mechanical stirrer and an addition funnel, was added 20 g (60% dispersion in oil, 0.5 mol) of sodium hydride, washed with three 25-mL portions of hexane, 400 mL of ethyl ether, and 50 mL (43.0 g, 0.31 mol) of triethylsilanol,[24] with evolution of gas. The resulting mixture was cooled to 0 °C, and 47.2 g (0.31 mol) of *N,N,N′,N′*-tetramethylphosphorodiamido chloride[23] in 100 mL of ether was added dropwise over 3 h with formation of a white precipitate. The resulting mixture was warmed to room temperature, stirred overnight and filtered under nitrogen. Fractional distillation gave 59.0 g (77%) of **17** as a clear, colorless liquid: bp 62–70 °C (0.003 mm); NMR (C_6D_6) δ 2.48 (d, 12, J_{PH} = 9.2 Hz, $P(NMe_2)_2$), 1.25–0.35 ppm (m, 15, Et_3Si).

Exact mass (75 eV) *m/e* calcd for $C_{10}H_{27}N_2OPSi$: 250.163. Found: 250.162.

Dimethyl 1-(Trimethylsilyloxy)-2-methylpropylphosphonate (18). A solution of 1.7 mL (1.73 g, 24 mmol) of isobutyraldehyde and 4.55 g (25 mmol) of silyl phosphite was prepared at 0 °C and allowed to warm to room temperature. Distillation afforded 5.02 g (82%) of phosphonate **18:** bp 52–58 °C (0.03 mm); IR (neat), 1250 (P=O, $SiMe_3$), 1180 [$P(OMe)_2$], 1050 and 1030 [$P(OMe)_2$, SiO], 840 and 750 cm^{-1} ($SiMe_3$); NMR (CCl_4) δ 3.55 [d, 6, J_{PH} = 10 Hz, $P(OMe)_2$], 3.53 (d of d, 1, J_{HH} = 7 Hz, SiOCHP), 2.10–1.43 (m, 1, Me_2CH), 0.98 (d, 6, J_{HH} = 7 Hz, CMe_2), and −0.03 ppm (s, 9, $SiMe_3$).

Anal. $C_9H_{23}O_4PSi$: C, 42.40; H, 9.21.

Dimethyl 1-(Trimethylsilyloxy)hexylphosphonate (19). A solution of 20 mL of benzene and 5.00 g (50 mmol) of 1-hexanal was cooled to 5 °C in an ice bath, and a solution of 8.92 g (49 mmol) of silyl phosphite **10** in 10 mL of benzene was added dropwise with stirring. Upon completion of addition, the flask was warmed to 25 °C and the reaction mixture stirred for 1 h. Removal of the solvent in vacuo followed by distillation gave 11.1 g (81%) of phosphonate **19:** bp 82–85 °C (0.03 mm); IR (neat) 1250 (P=O, $SiMe_3$), 1060 and 1030 [$P(OMe)_2$, SiO], 850 and 760 cm^{-1} ($SiMe_3$); NMR (CCl_4) δ 3.40 (m, 1, ≡CH), 3.28 [d of d, 6, J_{PH} = 10, J_D = 1 Hz, $P(OMe)_2$], 1.30–0.63 (m, 8, $-CH_2-$), 0.63–0.30 (m, 3, CH_3), and −0.33 ppm (s, 9, $SiMe_3$).

Anal. $C_{11}H_{27}O_4PSi$: C, 46.70; H, 9.62.

Dimethyl 1-(Trimethylsilyloxy)benzylphosphonate (20). To a solution of 20 mL of benzene and 5.43 g (51 mmol) of benzaldehyde was added 9.66 g (53 mmol) of silyl phosphite **10** in 10 mL of benzene with stirring over 0.5 h. Upon completion of addition the reaction mixture was stirred at 25 °C for 24 h. After removal of solvent in vacuo, distillation afforded 14.3 g (97%) of phosphonate **20:** bp 101–106 °C (0.03 mm); IR (neat) 1250 (P=O, $SiMe_3$), 1190 [$P(OMe)_2$], 1050 and 1030 [$P(OMe)_2$, SiO], 840 and 760 cm^{-1} ($SiMe_3$); NMR (CCl_4) δ 7.12 (broad s, 5, C_6H_5-), 4.73 (d, 1, J_{PH} = 15 Hz, SiOCH), 3.47 [d, 6, J_{PH} = 10 Hz, $P(OMe)_2$], and 0.02 ppm (s, 9, $SiMe_3$).

Anal. $C_{12}H_{21}O_4PSi$: C, 50.16; H, 7.32.

Dimethyl 1-(Trimethylsilyloxy)-1-methylethylphosphonate (21). In a pressure bottle equipped for magnetic stirring were placed 2.3 mL (1.76 g, 30 mmol) of acetone and 5.5 mL (5.03 g, 28 mmol) of silyl phosphite **10.** The contents was heated to 100 °C for 48 h. Analysis by NMR showed the reaction to be complete. Distillation of the reaction mixture afforded 4.97 g (64%) of phosphonate **21:** bp 50 °C (0.97 mm); IR (neat) 1250 (P=O, $SiMe_3$), 1070 and 1030 cm^{-1} [$P(OMe)_2$, Si–O]; NMR ($CDCl_3$) δ 3.80 [d, 6, J_{PH} = 10 Hz, $P(OMe)_2$], 2.93 (d, 6, J_{PH} = 16 Hz, CMe_2), and 0.17 ppm (s, 9, $SiMe_3$).

Anal. $C_8H_{21}O_4PSi$: C, 39.72; H, 8.76.

Dimethyl 1-(Trimethylsilyloxy)-1-methylhexylphosphonate (22). A solution of 3.4 mL (2.73 g, 24 mmol) of 2-heptanone and 4.35 g (24 mmol) of silyl phosphite **10** was stirred for 36 h at 95 °C whereupon NMR analysis indicated incomplete conversion. Distillation afforded 4.43 g (62%) of silyl phosphonate **22:** bp 80–85 °C (0.022 mm); IR (neat) 1250 (P=O, $SiMe_3$), 1060 and 1040 cm^{-1} [$P(OMe)_2$, Si–O]; NMR ($CDCl_3$) δ 3.75 [d, 6, J_{PH} = 10 Hz, $P(OMe)_2$], 1.80–1.13 (m, 8, $-CH_2-$), 1.46 (d, 3, J_{PH} = 15 Hz, CH_3CP), 1.50–0.63 (m, 3, CH_2CH_3), and 0.17 ppm (s, 9, $SiMe_3$).

Anal. $C_{12}H_{29}O_4PSi$: C, 48.79; H, 9.96.

Dimethyl 1-(Trimethylsilyloxy)cyclohexylphosphonate (23). A solution of 2.6 mL (2.56 g, 26 mmol) of cyclohexanone and 5.0 mL (4.76 g, 26 mmol) of silyl phosphite **10** was stirred for 13 h at 95 °C at which time NMR analysis showed 95% conversion to product. Upon cooling the product was distilled affording 6.3 g (86%) of silyl phosphonate **23:** bp 82–85 °C (0.035 mm); IR (neat) 1250 (P=O, $SiMe_3$), 1070 and 1030 cm^{-1} [$P(OMe)_2$, Si–O]; NMR ($CDCl_3$) δ 3.78 [d, 6, J_{PH}

= 11 Hz, $P(OMe)_2$], 2.03-1.30 (m, 10, $-CH_2-$), and 0.23 ppm (s, 9, $SiMe_3$).

Anal. $C_{11}H_{25}O_4PSi$: C, 47.05; H, 8.85.

Dimethyl 1-(*tert*-Butyldimethylsilyloxy)hexylphosphonate (24). A solution of 1.19 mL (1.00 g, 10 mmol) of 1-hexanal and 2.24 g (10 mmol) of silyl phosphite **16** was heated at 100 °C for 3 h; NMR analysis showed the reaction to be complete. After cooling, distillation from the reaction vessel afforded 2.6 g (81%) of silyl phosphonate **24:** bp 92-102 °C (0.01 mm); IR (neat) 1250 (P=O, $SiMe_2$), 1040 and 1060 cm^{-1} [$P(OMe)_2$, SiO]; NMR (CCl_4) δ 3.81 [d of d, 6, J_{PH} = 10.5, J_D = 1.5 Hz, $P(OMe)_2$], 2.05-1.08 (m, 12), 0.95 (s, 9, *t*-BuSi), and 0.18 ppm (d, 6, J_D = 3 Hz, $SiMe_3$).

Anal. $C_{14}H_{33}O_4PSi$: C, 51.58; H, 10.01.

Dimethyl 1-(*tert*-Butyldimethylsilyloxy)benzylphosphonate (25). A solution of 1.13 mL (1.17 g, 11 mmol) of benzaldehyde and 2.49 g (11 mmol) of silyl phosphite **16** was stirred for 6 h at 25 °C. The product was distilled from the reaction vessel giving 2.36 g (65%) of the siloxyphosphonate **25:** bp 123-130 °C (0.012 mm); IR (neat) 1250 (P=O, $SiMe_3$), 1050 $[P(OMe)_2]$, and 1030 cm^{-1} (Si-O); NMR (CCl_4) δ 7.25 [s (broad), 5, C_6H_5], 4.83 (d, 1, J_{PH} = 14 Hz, CHOSi), 3.54 [d of d, 6, J_{PH} = 11, J_D = 2 Hz, $P(OMe)_2$], 0.88 (s, 9, *t*-Bu), and 0.03 ppm (d, 6, J_D = 9 Hz, $SiMe_3$).

Anal. $C_{15}H_{27}O_4PSi$: C, 54.46; H, 8.19.

Dimethyl 1-(*tert*-Butyldimethylsilyloxy)-1-phenylethylphosphonate (26). A solution of 2.25 mL (2.32 g, 19 mmol) of acetophenone and 4.34 g (19 mmol) of silylphosphite **16** was heated for 48 h at 120 °C. After this time period the reaction mixture still contained 35% starting material. Distillation afforded 2.28 g (34%) of silyl phosphonate **26:** bp 128-135 °C (0.03 mm); IR (neat) 1260 (P=O, $SiMe_3$), 1060 and 1040 cm^{-1} [$P(OMe)_2$, SiO]; NMR ($CDCl_3$) δ 7.93-7.40 (m, 5, Ph), 3.82 [d of d, 6, J_{PH} = 10.5, J_D = 8 Hz, $P(OMe)_2$], 2.17 (d, 3, J_{PH} = 16 Hz, CH_3), 1.25 (s, 9, *t*-BuSi), and 0.07 ppm (d, 6, J_D = 8 Hz, $SiMe_3$).

Anal. $C_{16}H_{29}O_4PSi$: C, 55.33; H, 8.45.

***N,N,N',N'*-Tetramethyl-*P*-1-(triethylsilyloxy)benzylphosphonic Diamide (27).** To a cooled (0 °C) solution of 5 mL of diethyl ether and 4.79 g (19.2 mmol) of **17** was added 2.05 g (19.3 mmol) of benzaldehyde dropwise under an inert atmosphere. The ice bath was removed, and the reaction mixture allowed to warm to room temperature over 0.5 h. Removal of the solvent in vacuo followed by molecular distillation (190 °C, 0.003 mm) yielded 6.28 g (92%) of **27** as a colorless liquid: IR (neat) 1212 (P=O), 1062 (SiO), and 969 cm^{-1} (P-N); NMR (CCl_4) δ 7.29 (m, 5, Ph), 5.15 (d, 1, J_{PH} = 10.5 Hz, CHOSi), 2.54 (d, 6, J_{PH} = 9.5 Hz, $PNMe_2$), 2.49 (d, 6, J_{PH} = 7.5 Hz, $PNMe_2$), and 1.07-0.25 ppm (m, 15, $SiEt_3$).

Exact mass (75 eV) *m/e* calcd for $C_{17}H_{33}N_2O_2PSi$: 356.205. Found: 356.208.

***N,N,N',N'*-Tetramethyl-*P*-1-(triethylsilyloxy)hexylphosphonic Diamide (28).** To a cooled (0 °C) solution of 5 mL of diethyl ether and 4.81 g (19.2 mmol) of **17** was added 2.15 g (18.8 mmol) of 1-heptanal dropwise. The ice bath was removed, and the reaction mixture allowed to warm to room temperature over 0.5 h. Removal of the solvent in vacuo followed by molecular distillation (200 °C, 0.001 mm) yielded 6.69 g (97%) of **28** as a colorless liquid: IR (neat) 1200 (P=O), 1092 (SiO), 992 cm^{-1} (P-N); NMR (CCl_4) δ 4.00 (m, 1, methine), 2.65 (d, 6, J_{PH} = 8.4 Hz, $PNMe_2$), 2.59 (d, 6, J_{PH} = 9.7 Hz, $PNMe_2$), and 1.67-0.33 ppm (m, 28, alkyl $SiEt_3$).

Exact mass (75 eV) *m/e* calcd for $C_{17}H_{41}N_2O_2PSi$: 364.267. Found: 364.268.

***N,N,N',N'*-Tetramethyl-*P*-1-(triethylsilyloxy)ethylphosphonic Diamide (29).** To a cooled (0 °C) solution of 5 mL of diethyl ether and 4.81 g (19.2 mmol) of **17** was added 1.2 mL (0.94 g, 21.3 mmol) of acetaldehyde dropwise. The ice bath was removed, and the reaction mixture allowed to warm to room temperature over 0.5 h with formation of a black precipitate. The reaction mixture was dissolved in CCl_4, filtered, and concentrated in vacuo to yield a brown oil which was molecularly distilled (175 °C, 0.15 mm) to yield 4.68 g (83%) of adduct **29:** IR (neat) 1202 (P=O), 1082 (SiO), 997 cm^{-1} (PN); NMR (CCl_4) δ 4.28 (d of q, 1, J_{PH} = 7, J_{HH} = 7 Hz, methine), 2.70 (d, 6, J_{PH} = 8.2 Hz, $PNMe_2$), 2.60 (d, 6, J_{PH} = 9.6 Hz, $PNMe_2$), 1.38 (d of d, 3, J_{PH} = 15.5, J_{HH} = 7 Hz, CH_3), and 1.16-0.33 ppm (m, 15, $SiEt_3$).

Exact mass (75 eV) *m/e* calcd for $C_{12}H_{31}N_2O_2PSi$: 294.189. Found: 294.190.

Crossover Experiments with Benzaldehyde, 12, and 16. To a flask equipped with serum cap and magnetic stirrer were added 5.61 g (25 mmol) of dimethyl *tert*-butyldimethylsilyl phosphite (**16**) and 5.78 g (25 mmol) of diethyl trimethylsilyl phosphite (**12**). The mixture was cooled in an ice bath, and 5.08 mL (5.31 g, 50 mmol) of benzaldehyde was added via syringe. The mixture was allowed to warm to room temperature and was stirred for 10 h. Distillation gave 14.60 g (90%) of a colorless oil: bp 110-125 °C (0.06 mm) [lit.,[25a] bp 124-125 °C (1-1.5 mm) for diethyl 1-(trimethylsilyloxy)benzylphosphonate (**30**) and 123-130 °C (0.012 mm) for dimethyl 1-(*tert*-butyldimethylsilyloxy)benzylphosphonate (**25**)]: NMR (CCl_4) δ 7.67-7.23 (m, 10, 2 Ph), 5.04 (d, 1, J_{PH} = 15 Hz, methine), 5.01 (d, 1, J_{PH} = 15 Hz, methine), 4.08 (d of q, 4, J_{HH} = 7, J_{PH} = 7 Hz, $-OCH_2CH_3$), 3.68 [d of d, 6, J_{PH} = 11, J_D = 1.5 Hz, $P(OMe)_2$], 1.25 (t, 6, J_{HH} = 6 Hz, $-OCH_2CH_3$), 0.97 (s, 9, *t*-BuSi), 0.13 (s, 9, $SiMe_3$), 0.03 (s, 6, $SiMe_3$). Analysis by GLC indicated that two compounds were present in the reaction mixture in equal quantities (2 m, 5% SE-30 on Chromosorb W AW DMCS, 130-250 °C, 10 °C/min, flow 30 mL/min). The two components were separated by preparative GLC (2 m, 10% SE-30 on Chromosorb W AW DMCS, 200 °C, flow 80 mL/min). The faster moving component (7 min) was **30**, and the slower (12 min) was **25**. The isolated products contained no material from intermolecular silicon transfer. One crossover product, **20**, prepared previously, was shown to be absent in the reaction mixture. Mass spectral analysis showed the presence of fragments of *m/e* 272 and below (75 and 12 eV). The expected molecular ions for the initial products **25** (*m/e* 330) and **30** (*m/e* 316) were not present, nor were the molecular ions for products from intermolecular silicon migration **20** (*m/e* 288) and diethyl 1-(*tert*-butyldimethylsiloxy)benzylphosphonate **31** (*m/e* 358).

The above experiment was repeated using 5.61 g (25 mmol) of **16**, 5.78 g (25 mmol) of **12**, and 2.54 mL (2.65 g, 25 mmol) of benzaldehyde. The distilled product (8.30 g) was a 4.1:1 (GLC) mixture of **30** and **25**, bp 112-120 °C (0.055 mm). Analysis by GLC and NMR gave no evidence for the presence of crossover products.

The above experiment was repeated using 0.42 g (2 mmol) of **12**, 2.24 g (10 mmol) of **16**, and 1.02 mL (1.06 g, 10 mmol) of benzaldehyde. The distilled product (2.78 g) was a 1:3.3 (GLC) mixture of **30** and **25**, bp 112-125 °C (0.06 mm). Analysis by GLC and NMR gave no evidence for the presence of crossover products.

Dimethyl 1-(Trimethylsilyloxy)-2-propenylphosphonate (35). A. From Dimethyl 1-Hydroxy-2-propenylphosphonate. To a flask equipped with reflux condenser and magnetic stirrer were added 50 mL of THF, 5.0 mL (6.0 g, 54 mmol) of dimethyl phosphite, and 3.6 mL (3.0 g, 54 mmol) of acrolein. The reaction mixture was cooled, and 10 mg of sodium hydride was added cautiously with gas evolution. The reaction mixture was refluxed for 3 h at which time NMR analysis showed completion conversion to product. The reaction mixture was poured into 100 mL of methylene chloride, and the organic material washed with 5 mL of saturated ammonium chloride solution and 10 mL of brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated to 8.28 g of a pale yellow oil. Molecular distillation (100 °C, 0.002 mm) gave 6.54 g (72%) of dimethyl 1-hydroxy-2-propenylphosphonate as a colorless oil: IR (neat), 3300 (-OH), 1635 (C=C), 1240 (P=O), 1180 $[P(OMe)_2]$, 930 and 1000 cm^{-1} ($-CH=CH_2$); NMR ($CDCl_3$) δ 6.42-5.78 (m, 1, vinyl H), 5.78-5.12 (m, 3, vinyl H, OH), 4.88-4.33 (m, 1, SiOCHP), and 3.83 [d, 6, J_{PH} = 10.5 Hz, $P(OMe)_2$].

In a NMR tube was placed 0.832 g (5.0 mmol) of dimethyl 1-hydroxy-2-propenylphosphonate and 1.26 mL (0.99 g, 10.0 mmol) of trimethylsilyl cyanide.[47] After the initial exothermic reaction had subsided (~10 min), NMR analysis indicated complete reaction. The excess silyl cyanide was removed in vacuo, and molecular distillation (50 °C and 0.002 mm) afforded 1.06 g (89%) of phosphonate **35:** IR (neat) 1630 (C=C), 1245 (P=O, $SiMe_3$), 1175 $[P(OMe)_2]$, 1050 and 1030 $[P(OMe)_2, SiO]$, 985 and 915 ($-CH=CH_2$), 840 and 750 cm^{-1} ($SiMe_3$); NMR ($CDCl_3$) δ 6.17-5.53 (m, 1, vinyl H), 5.45-4.90 (m, 2, vinyl H), 4.33 (d of d of d of d, 1, J_{PH} = 16, J_{HH} = 5, J_{HH} = 1.5, J_{HH} = 1.5 Hz, SiOCHP), 3.82 [d, 6, J_{PH} = 10 Hz, $P(OMe)_2$], and 0.17 ppm (s, 9, $SiMe_3$).

Exact mass (75 eV) *m/e* calcd for $C_9H_{19}O_4PSi$: 238.079. Found: 238.079.

B. From Acrolein and 10 (Method A). In a flask equipped with magnetic stirrer and nitrogen inlet was placed 4.92 g (27.0 mmol) of silyl phosphite **10.** The flask was cooled in an ice bath, and 1.80 mL (1.51 g, 27.0 mmol) of acrolein was added. The ice bath was removed, and the reaction mixture allowed to warm to room temperature and stir for 12 h. Fractional distillation gave 5.68 g (88%) of dimethyl

1-(trimethylsilyloxy)-2-propenylphosphonate (**35**) and a mixture of olefin isomers of dimethyl 3-(trimethylsilyloxy)-2-propenylphosphonate (**36**) in a ratio of 47:53, bp 50–64 °C (0.01 mm).

Separation by preparative GLC gave pure samples of **35** and **36** (15% SE-30 on Chromosorb W, 190 °C, flow 80 mL/min). For **36:** IR ($CDCl_3$) 1645 (C=C), 1250 (P=O, $SiMe_3$), 1050 and 1025 cm^{-1} [$P(OMe)_2$, SiO]; NMR ($CDCl_3$) δ 6.29 (d of d of t, 1, J_{PH} = 5, J_{HH} = 6, J_{HH} = 1.5 Hz, *Z* isomer, =CHOSi), 4.49 (d of d of d, 1, J_{HH} = 7.5, J_{HH} = 6, J_{PH} = 6 Hz, *Z* isomer, -CH=), 3.68 [d, 6, J_{PH} = 10.5 Hz, *Z* isomer, $P(OMe)_2$], 2.60 (d of d of d, 2, J_{PH} = 22.5, J_{HH} = 7.5, J_{HH} = 1.5 Hz, *Z* isomer, $-CH_2-$), 2.43 (d of d, 2, J_{PH} = 21, J_{HH} = 8 Hz, *E* isomer, $-CH_2-$), 0.19 (s, 9, *E* isomer, $SiMe_3$), and 0.13 ppm (s, 9, *Z* isomer, $SiMe_3$).

Exact mass (75 eV) *m/e* calcd for $C_8H_{19}O_4PSi$: 238.079. Found: 238.081.

Dimethyl 1-(Trimethylsilyloxy)-2-propenylphosphonate (35) (Method B). In a flask equipped for magnetic stirring were placed 5.3 mL (5.57 g, 45 mmol) of trimethyl phosphite and 5.7 mL (4.88 g, 45 mmol) of trimethylchlorosilane. The mixture was cooled in an ice bath, and 3.0 mL (2.52 g, 45 mmol) of acrolein was added dropwise. The exothermic reaction was accompanied by a vigorous evolution of methyl chloride. After 4 h at 25 °C, distillation afforded 7.50 g (70%) of alkylphosphonate **35**, bp 61–65 °C (0.97 mm), whose physical and spectral properties were identical with those reported above.

***N,N,N',N'*-Tetramethyl-*P*-1-(triethylsilyloxy)-2-propenylphosphonic Diamide (37).** A solution of 5 mL of THF and 1.89 g (7.55 mmol) of **17** was cooled with an ice bath, and 0.50 mL (0.42 g, 7.50 mmol) of acrolein was added. The cooling bath was removed, and the reaction mixture allowed to warm to 25 °C over a 15-min period. After removal of solvent in vacuo, molecular distillation (180 °C, 0.007 mm) yielded 2.07 g (90%) of **37** as a pale yellow liquid: IR (neat) 1651 and 1633 (C=C), 1214 (P=O), 1061 (Si-O), and 994 cm^{-1} (P-N); NMR (CCl_4) δ 6.52–5.03 (m, 3, vinyl H), 4.90–4.42 (m, 1, methine), 2.60 (d, 6, J_{PH} = 8.3 Hz, $PNMe_2$), 2.55 (d, 6, J_{PH} = 9.5 Hz, $PNMe_2$), and 1.27–0.37 ppm (m, 15, $SiEt_3$).

Exact mass (75 eV) *m/e* calcd for $C_{13}H_{31}N_2O_2PSi$: 306.189. Found: 306.190.

(*Z*)-3-(Triethylsilyloxy)-2-propenyldiphenylphosphine Oxide (38). A solution of 15 mL of benzene, 5.0 mL (5.52 g, 25.5 mmol) of methyl diphenylphosphinite,[48] and 4.29 mL (3.85 g, 25.5 mmol) of triethylchlorosilane was cooled in an ice bath, and 1.70 mL (1.43 g, 25.5 mmol) of acrolein was added. The ice bath was removed, and the reaction mixture allowed to stir at 25 °C for 2 h. Removal of the solvent in vacuo left 9.46 g (NMR crude yield 100%) of a pale yellow, viscous oil, **38.** Attempted distillation resulted in decomposition: IR (CCl_4) 3050 (aromatic), 1645 (C=C), 1185 (P=O), 1090 (SiO), and 685 cm^{-1} (cis C=C); NMR ($CDCl_3$) δ 8.03–7.13 (m, 10, Ph), 6.27 (d of t of d, 1, $J_{HC=CH}$ = 6, J_{HH} = 7.5, J_{PH} = 6 Hz, -CH=), 3.22 (d of d of t, 2, J_{PH} = 14.5, J_{HH} = 7.5, $J_{HCC=CH}$ = 1 Hz, methylene), and 1.17–0.30 ppm (m, 15, $SiEt_3$).

Exact mass (75 eV) *m/e* calcd for $C_{21}H_{29}O_2PSi$: 372.167. Found: 372.169.

(*Z*)-3-(Trimethylsilyloxy)-2-propenyltriphenylphosphonium Chloride (39). In a dry, nitrogen-purged, centrifuge tube was placed 0.262 g (1.0 mmol) of triphenylphosphine. Benzene (3 mL) was added, and the container sealed with a serum cap. Trimethylchlorosilane (0.13 mL, 0.108 g, 1.0 mmol) was added slowly creating a faint turbidity in the solution. After mixing, acrolein was added dropwise causing a small amount of a fluffy, white precipitate. Upon standing for ca. 15 min, an oil began to separate from the reaction mixture. Upon decantation of the supernatant and removal of the remaining solvent in vacuo, 705 mg of a white foam remained. Examination by NMR revealed the presence of benzene in the product which could not be removed by further vacuum treatment: IR ($CDCl_3$) 1640 (C=C), 1250 ($SiMe_3$), and 1030 cm^{-1} (SiO); NMR ($CDCl_3$) δ 7.98–7.34 (m, 15, Ph), 7.24 (s, C_6H_6), 6.28 (broad d of d, 1, J_{PH} = 6, J_{HH} = 6 Hz, =CHO-), 4.78–4.08 (m, 3, $-CH_2CH=$), and −0.03 ppm (s, 9, $SiMe_3$).

Attempted purification resulted in hydrolysis of the silyl enol ether to form 3-oxopropyltriphenylphosphonium chloride: IR ($CDCl_3$) 1715 cm^{-1} (C=O); NMR ($CDCl_3$) δ 9.67 (s, 1, CHO), 8.00–7.42 (m, 15, Ph), 3.72 (d of t, 2, J_{PH} = 12, J_{HH} = 6 Hz, CH_2), and 3.08 ppm (d of t, 2, J_{PH} = 14, J_{HH} = 6 Hz).

(*Z*)-3-(Trimethylsilyloxy)-2-methyl-2-propenyltriphenylphosphonium Chloride (40). In a dry, nitrogen-flushed centrifuge tube was placed 0.588 g (2.2 mmol) of triphenylphosphine. Benzene (3 mL) was added, and the container sealed with a serum cap. Trimethylchlorosilane (0.284 mL, 244 mg, 2.2 mmol) was added slowly creating a faint turbidity in the solution. After mixing, 0.198 mL (168 mg, 2.2 mmol) of methacrolein was added dropwise causing a small amount of a fluffy white precipitate to form. Upon standing for 2 h at room temperature, a voluminous precipitate had separated from solution. Upon decantation of the supernatant and removal of the remaining solvent in vacuo, 1.26 g of a white solid remained. Examination by NMR revealed the presence of benzene which could not be removed by further vacuum treatment: IR (CD_3CN) 1660 (C=C), ($SiMe_3$), and 1030 cm^{-1} (SiO); NMR (CD_3CN) δ 8.15–7.67 (m, 15, Ph), 6.30 (d, 1, J_{PH} = 6 Hz, =CH), 4.29 (d, 2, J_{PH} = 15 Hz, $-CH_2-$), 1.38 (broad s, 3, CH_3), and −0.08 ppm (s, 9, $SiMe_3$).

Attempted purification resulted in hydrolysis of the silyl enol ether to form 3-oxo-2-methylpropyltriphenylphosphonium chloride: IR (CD_3CN) 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ 9.50 (s, 1, CHO), 8.00–9.30 (m, 15, Ph), 4.63–3.60 (m, 1, methine), 3.33–2.77 (m, 2, CH_2), 1.37 (d of d, 3, J_{PH} = 8, J_{HH} = 8 Hz, CH_3).

Reaction between Crotonaldehyde and 10. A solution of 7.58 g (41.6 mmol) of silyl phosphite **10** and 3.4 mL (2.91 g, 41.6 mmol) of crotonaldehyde was heated to 55 °C for 18 h. Fractional distillation yielded 9.46 g (19%) of dimethyl (*Z*)-1-(trimethylsilyloxy)-2-butenylphosphonate (**41**) and a mixture of olefin isomers of dimethyl 3-(trimethylsilyloxy)-1-methyl-2-propenylphosphonate (**42**) in a ratio of 75:25, bp 64–65 °C (0.006 mm).

Dimethyl (*Z*)-1-(Trimethylsilyloxy)-2-butenylphosphonate (41). In a reaction vessel were placed 3.26 mL (2.80 g, 40.0 mmol) of crotonaldehyde, 4.71 mL (4.96 g, 40.0 mmol) of trimethyl phosphite, and 5.07 ml (4.34 g, 40 mmol) of trimethylchlorosilane. The reaction vessel was sealed and heated at 55 °C for 3 h and cooled to 25 °C, and the methyl chloride by-product vented in a fume hood. Fractional distillation yielded 6.22 g (62%) of **41:** bp 67–69 °C (0.06 mm); IR (neat) 1670 (C=C), 1250 (P=O), 1040 [$P(OMe)_2$, SiO], and 970 cm^{-1} (trans C=C); NMR ($CDCl_3$) δ 6.00–5.47 (m, 2, CH=CH), 4.58 (d of d, 1, J_{PH} = 12, J_{HH} = 5 Hz, methine), 3.77 [d of d, 6, J_{PH} = 10, J_D = 2 Hz, $P(OMe)_2$], 1.77 (d of d, 3, J_{PH} = 5, J_{HH} = 5 Hz, CH_3), and 0.20 ppm (s, 9, $SiMe_3$).

Anal. $C_9H_{21}O_4PSi$: C, 42.83; H, 8.38.

Independent Synthesis of Dimethyl 3-(Trimethylsilyloxy)-1-methyl-2-propenylphosphonate (42). A. Methyl 3-(Dimethoxyphosphinyl)-propanoate. Into a dry flask equipped with a magnetic stirrer, nitrogen inlet, and reflux condenser were placed 50 mL of THF and ca. 20 mg of sodium hydride in an oil dispersion. Dimethyl phosphite (5.0 mL, 6.00 g, 54.0 mmol) was added followed by 5.7 mL (5.40 g, 54.0 mmol) of methyl crotonate. The reaction mixture was heated at reflux for 3 h, poured into 30 mL of brine, and extracted with three 100-mL portions of diethyl ether. The organic material was dried (Na_2SO_4), filtered, and concentrated in vacuo. Distillation afforded 8.21 g (72%) of methyl 3-(dimethoxyphosphinyl)propanoate: bp 76 °C (0.03 mm); IR (neat) 1740 (C=O), 1250 (P=O), and 1060 cm^{-1} [$P(OMe)_2$]; NMR ($CDCl_3$) δ 3.17 [d, 6, J_{PH} = 11 Hz, $P(OMe)_2$], 3.65 (s, 3, OCH_3), 2.93–2.10 (m, 4, CH_2CH), and 1.24 ppm (d of d, 3, J_{PH} = 18, J_{HH} = 6 Hz, CH_3).

Anal. $C_7H_{15}O_5P$: C, 40.08; H, 7.04.

B. Dimethyl 1-Methyl-3-oxopropylphosphonate. Into a dry flask equipped with nitrogen inlet and serum cap was distilled 400 mL of methylene chloride from calcium hydride. Methyl 3-(dimethoxyphosphinyl)propanoate (16.59 g, 78.9 mmol) was added, and the reaction mixture cooled to −65 °C in a dry ice-2-propanol bath. Diisobutylaluminum hydride (29.5 mL, 23.5 g, 165.7 mmol) was added slowly via syringe keeping the temperature below −60 °C. Upon completion of the addition, the reaction mixture was stirred at −65 °C for 3 h and quenched by the addition of 250 mL of 1 N HCl. The desired product was isolated by ether extraction. Distillation yielded 2.49 g (18%) of the desired aldehyde, dimethyl 1-methyl-3-oxopropylphosphonate: bp 78–79 °C (0.08 mm); IR (neat) 2750, 2870 (-CHO), 1725 (C=O), 1250 (P=O), and 1050 cm^{-1} [$P(OMe)_2$]; NMR ($CDCl_3$) δ 9.72 (m, 1, CHO), 3.74 [d, 6, J_{PH} = 11 Hz, $P(OMe)_2$], 3.27–2.17 (m, 3, CH_2CH), and 1.21 ppm (d of d, 3, J_{PH} = 17, J_{HH} = 6 Hz, CH_3).

Anal. $C_6H_{13}O_4P$: C, 40.20; H, 7.22.

C. Preparation of 42. The aldehyde prepared as described above was silylated according to the procedure of House[37] to give **42:** NMR ($CDCl_3$) δ 9.90 (m, 1, CHO), 6.28 (d of d, 1, J_{PH} = 5, J_{HH} = 5 Hz, *Z* isomer, -CH=), 4.73 (m, 2, CH_2), 3.77 [d, 6, J_{PH} = 10 Hz, $P(OMe)_2$], 3.75 [d, 6, J_{PH} = 10 Hz, $P(OMe)_2$], 3.23–2.42 (m, 3, $CHCH_2$), 1.58–0.98 (m, 6, CH_3), and 0.23 ppm (s, 9, $SiMe_3$).

Attempted Thermal Equilibration of 41. In dry, nitrogen-purged ampules made from 4-mm Pyrex tubing were placed ca. 200-mg samples of allylic phosphonate **41.** The ampules were sealed and heated in an oil bath. The progress of the reaction could be monitored by obtaining NMR spectra of the contents of the ampule and returning it to the heating bath. No isomerization was observed after 24 h at 50 °C, 24 h at 100 °C, and 24 h at 150 °C. The samples heated to 200 °C began a slow decomposition that continued after 37 h. However, no isomerization was noted.

Attempted Thermal Equilibration of 42. In a dry, nitrogen-purged ampule made from 4-mm Pyrex tubing was placed ca. 200 mg of silyl enol ether **42** and its parent aldehyde. The ampule was sealed and heated in an oil bath. The progress of the reaction was monitored by its NMR spectrum. No isomerization was observed after 17 h at 95 °C.

***N,N,N′,N′*-Tetramethyl-*P*-(*Z*)-1-(triethylsilyloxy)-2-butenylphosphonic Diamide (43).** A solution of 1.93 g (7.70 mmol) of **17** in 10 mL of THF was cooled in an ice bath. Crotonaldehyde (540 mg, 7.64 mmol) was added and the reaction mixture was allowed to warm to ambient temperature over 0.5 h. After removal of solvent in vacuo, molecular distillation (190 °C, 0.005 mm) yielded 2.23 g (95%) of **43** as an amber liquid: IR (neat) 1657 (C=C), 1217 (P=O), 1052 (SiO), 990 (P-N), and 968 cm^{-1} (trans C=C); NMR (CCl_4) δ 5.63 (m, 2, CH=CH), 4.55 (m, 1, methine), 2.65 (d, 6, J_{PH} = 8 Hz, $PNMe_2$), 2.58 (d, 6, J_{PH} = 9.5 Hz, $PNMe_2$), 1.75 (m, 3, CH_3), and 1.33-0.33 ppm (m, 15, $SiEt_3$).

Exact mass (75 eV) *m/e* calcd for $C_{14}H_{33}N_2O_2PSi$: 320.205. Found: 320.207.

***N,N,N′,N′*-Tetramethyl-*P*-(*Z*)-1-(triethylsilyloxy)-3-phenyl-2-propenylphosphonic Diamide (44).** A solution of 5 mL of THF and 3.09 g (12.4 mmol) of **17** was cooled in an ice bath, 15.6 mL (1.64 g, 12.4 mmol) of cinnamaldehyde was added, and the reaction mixture was allowed to warm to room temperature over 0.5 h. After removal of solvent in vacuo, molecular distillation (210 °C, 0.003 mm) yielded 4.42 g (93%) of **44** as an amber liquid: IR (neat) 1670 (C=C), 1211 (P=O), 1063 (SiO), 990 (P-N), and 970 cm^{-1} (trans C=C); NMR (CCl_4) δ 7.28 (m, 5, aromatic), 6.68-6.40 (m, 2, CH=CH), 4.88 (d of d, 1, J_{PH} = 15, J_{HH} = 4.5 Hz, methine), 2.68 (d, 6, J_{PH} = 8.7 Hz, $PNMe_2$), 2.62 (d, 6, J_{PH} = 9.5 Hz, $PNMe_2$), and 1.28-0.39 ppm (m, 15, $SiEt_3$).

Exact mass (75 eV) *m/e* calcd for $C_{19}H_{35}N_2O_2PSi$: 382.220. Found: 382.218.

Dimethyl(*Z*)-3-(Trimethylsilyloxy)-2-butenylphosphonate (45). Method A. A solution of 5.61 mL (4.86 g, 69.0 mmol) of methyl vinyl ketone and 12.62 g (69.0 mmol) of silyl phosphite **10** was heated for 6 h at 50 °C. Upon cooling, distillation yielded 15.40 g (88%) of **45** as a colorless liquid: bp 80-81 °C (0.20 mm); IR (neat) 1675 (C=C), 1255 (P=O), 1040 cm^{-1} [$P(OMe)_2$, SiO]; NMR (CCl_4) δ 4.53 (d, of t, 1, J_{PH} = 7, J_{HH} = 7 Hz, =CH), 3.73 [d, 6, J_{PH} = 10 Hz, $P(OMe)_2$], 2.57 (d of d, 2, J_{PH} = 20.5, J_{HH} = 7 Hz, $-CH_2-$), 1.83 (broad d, 3, J_{PH} = 5 Hz, CH_3), and 0.27 ppm (s, 9, $SiMe_3$).

Anal. $C_9H_{21}O_4PSi$: C, 42.70; H, 8.32.

Method B. In a dry pressure bottle were placed 8.10 mL (7.00 g, 100 mmol) of methyl vinyl ketone, 11.80 mL (12.40 g, 100 mmol) of trimethyl phosphite, and 12.68 mL (10.86 g, 100 mmol) of trimethylchlorosilane. The bottle was sealed, and the reaction mixture heated to 100 °C for 2 h. After the contents was cooled to room temperature and the methyl chloride by-product was vented in a fume hood, fractional distillation yielded 20.64 g (79%) of **45** as a colorless liquid whose properties were identical with those reported above.

Dimethyl (*Z*)-3-(Triethylsilyloxy)-2-butenylphosphonate (46). Method A. A pressure bottle was charged with 9.69 g (49.5 mmol) of silyl phosphite **14** and 4.0 mL (3.46 g, 49.5 mmol) of methyl vinyl ketone and the contents heated to 100 °C for 3 h. After cooling to room temperature, fractional distillation gave 5.07 g (36%) of **46** as a colorless liquid: bp 110-111 °C (0.05 mm); IR (neat) 1675 (C=C), 1268 (P=O), and 1060 cm^{-1} [$P(OMe)_2$, SiO]; NMR (CCl_4) δ 4.42 (d of t, 1, J_{PH} = 7, J_{HH} = 7 Hz, =CH), 3.67 [d, 6, J_{PH} = 11 Hz, $P(OMe)_2$], 2.52 (d of d, 2, J_{PH} = 20, J_{HH} = 7 Hz, $-CH_2-$), 1.84 (broad d, 3, J_{PH} = 5 Hz, CH_3), and 1.26-0.42 ppm (m, 15, $SiEt_3$).

Exact mass (75 eV) *m/e* calcd for $C_{12}H_{27}O_4PSi$: 294.141. Found: 294.144.

Method B. A dry pressure bottle was charged with 11.8 mL (12.4 g, 100 mmol) of trimethyl phosphite, 8.1 mL (7.0 g, 100 mmol) of methyl vinyl ketone, and 16.7 mL (15.1 g, 100 mmol) of triethylchlorosilane. The vessel was sealed, and the contents heated to 100 °C for 2 h. Distillation afforded 22.2 g (76%) of **46** as a colorless liquid whose properties were identical with those reported above.

***N,N,N′,N′*-Tetramethyl-*P*-(*Z*)-3-(triethylsilyloxy)-2-butenylphosphonic Diamide (47).** A solution of 5 mL of THF and 0.88 g (3.5 mmol) of **17** was cooled in an ice bath, and 0.29 mL (0.25 g, 3.6 mmol) of methyl vinyl ketone was added. The ice bath was removed, and the reaction mixture allowed to warm to room temperature over 0.5 h. Removal of the solvent in vacuo followed by molecular distillation (170 °C, 0.005 mm) afforded 0.92 g (82%) of adduct **47** as a pale yellow liquid: IR (neat) 1670 (C=C), 1210 (P=O), and 990 cm^{-1} (P-N); NMR (CCl_4) δ 4.50 (d of t, 1, J_{PH} = 6.5 J_{HH} = 6.5 Hz, =CH), 2.58 [d, 12, J_{PH} = 9.5 Hz, $P(NMe_2)_2$], 1.84 (broad d, 3, J_{PH} = 4 Hz, CH_3), and 1.25-0.42 ppm (m, 15, $SiEt_3$).

Exact mass (75 eV) *m/e* calcd for $C_{14}H_{33}N_2O_2PSi$: 320.205. Found: 320.203.

(*Z*)-3-(Triethylsilyloxy)-2-butenyldiphenylphosphine Oxide (48). To a solution of 8.71 g (40.2 mmol) of methyl diphenylphosphinite[48] and 6.77 mL (6.07 g, 40.2 mmol) of triethylchlorosilane under argon was added dropwise 3.26 mL (2.82 g, 40.2 mmol) of methyl vinyl ketone. After a 1-min induction period, an exothermic reaction ensued with the flask temperature reaching 80-100 °C. Upon completion of addition, the reaction mixture was allowed to cool to room temperature (0.5 h). Attempted fractional distillation (bath temperature up to 230 °C, 0.4 mm) and molecular distillation (150 °C, 0.005 mm) resulted in decomposition: IR (neat) 1668 (C=C), 1205 (P=O), and 1002 cm^{-1} (SiO); NMR ($CDCl_3$) δ 8.10-7.08 (m, 10, Ph), 4.56 (d of t, 1, J_{PH} = 7, J_{HH} = 7 Hz, -CH=), 3.14 (broad d of d, 2, J_{PH} = 14.5 Hz, $-CH_2-$), 1.73 (broad d, 3, J_{PH} = 4 Hz, CH_3), and 1.20-0.37 ppm (m, 15, $SiEt_3$).

Exact mass (75 eV) *m/e* calcd for $C_{22}H_{31}O_2PSi$: 386.183. Found: 386.186.

(*Z*)-3-(Trimethylsilyloxy)-2-butenyltriphenylphosphonium Chloride (49). Into a dry flask equipped with a magnetic stirrer were placed 300 mL of benzene and 13.1 g (50 mmol) of triphenylphosphine, followed by 6.34 mL (5.43 g, 50 mmol) of trimethylchlorosilane and 4.05 mL (3.50 g, 50 mmol) of methyl vinyl ketone. The reaction mixture was stirred for 5 h at room temperature by which time a voluminous precipitate of phosphonium salt had formed. The precipitate was filtered under nitrogen, then placed under high vacuum to remove traces of solvent to yield 17.92 g of **49** as a white solid contaminated with ca. 5% of ketone arising from hydrolysis: IR ($CDCl_3$) 1660 (C=C), 1260 ($SiMe_3$), and 1020 cm^{-1} (SiO); NMR ($CDCl_3$) δ 8.02-7.42 (m, 15, Ph), 4.68-4.02 (m, 3, CH_2CH=), 1.72 (broad d, 3, J_{PH} = 5 Hz, CH_3), and 0.07 ppm (s, 15, $SiMe_3$). Attempted mass spectral analysis resulted in fragmentation to starting materials.

Attempted purification resulted in hydrolysis to 3-oxobutyltriphenylphosphonium chloride: IR ($CDCl_3$) 1715 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.03-7.42 (m, 15, Ph), 3.98 (d of d, 2, J_{PH} = 13, J_{HH} = 6 Hz, $-CH_2-$), 3.15 (d of d, 2, J_{PH} = 16, J_{HH} = 6 Hz, $-CH_2-$), and 1.25 ppm (s, 3, CH_3).

Dimethyl (*Z*)-3-(Trimethylsilyloxy)-1-methyl-2-butenylphosphonate (50). A solution of 4.84 g (26.5 mmol) of silyl phosphite **10** and 2.59 mL (2.23 g, 26.5 mmol) of 3-penten-2-one was heated at 80 °C for 24 h. Fractional distillation afforded 4.47 (64%) of **50:** bp 67-68 °C (0.06 mm); IR (neat) 1675 (C=C), 1250 (P=O, $SiMe_3$), and 1050 cm^{-1} [$P(OMe)_2$, SiO]; NMR ($CDCl_3$) δ 4.47 (d of d, 1, J_{PH} = 5, J_{HH} = 6 Hz, =CH), 3.75 [d, 6, J_{PH} = 11 Hz, $P(OMe)_2$], 2.50-2.32 (m, 1, methine), 1.87 (d, 3, J_{PH} = 5 Hz, CH_3), 1.20 (d of d, 3, J_{PH} = 18, J_{HH} = 7 Hz, CH_3), and 0.23 ppm (s, 9, $SiMe_3$).

Anal. $C_{10}H_{23}O_4PSi$: C, 44.99; H, 8.55.

Olefin Isomerization of 46. A mixture of 2.879 g (9.8 mmol) of **46** and 10 mg of triethylamine hydrochloride was heated at 120-140 °C for 6 h, cooled to room temperature, and poured into 150 mL of hexane-ether (2:1). The organic material was extracted once with 5 mL of H_2O and once with 10 mL of brine, dried (Na_2SO_4), and concentrated in vacuo to 2.085 g of an oil. Fractional distillation gave 508 mg of a mixture of **46Z** and **46E**, and a terminal olefin isomer in a ratio of 60:35:5: bp 100-110 °C (0.04 mm); IR 1668 and 1655 (C=C), 1250 (P=O), 1050 and 1030 cm^{-1} [$P(OMe)_2$, SiO]; NMR (C_6D_6) *Z* isomer δ 4.53 (d of t, 1, J_{PH} = 7.5, J_{HH} = 7.5 Hz, =CH-), 3.53 [d, 6, J_{PH} = 11 Hz, $P(OMe)_2$], 2.67 (d of d, 2, J_{PH} = 22, J_{HH} = 7.5 Hz, $-CH_2-$), 1.74 (broad d, 3, J_{PH} = 6 Hz, CH_3), and 2.33-0.33 ppm (m, 15, $SiEt_3$); *E* isomer δ 4.80 (d of t, 1, J_{PH} = 8, J_{HH} = 8 Hz, =CH-), 3.53 [d, 6, J_{PH} = 11 Hz, $P(OMe)_2$], 2.36 (broad d of d, 2, J_{PH} = 21.5, J_{HH} = 8.5 Hz, $-CH_2-$), 1.68 (broad d, 3, J_{PH} = 5 Hz, CH_3), and 2.22-0.33 ppm (m, 15, $SiEt_3$).

This material was used directly for the ^{13}C NMR experiments.

2,2,2-Trimethoxy-2,2-dihydro-5-methyl-1,2-oxaphosphol-4-ene (58). The title compound was prepared by the procedure of Westheimer[43a] from methyl vinyl ketone and trimethyl phosphite in 53% yield, bp 77–80 °C (5 mm).

Reaction of 58 with Trimethylchlorosilane. A dry NMR tube was charged with 428 mg (2.21 mmol) of oxaphospholene **58.** Trimethylchlorosilane (0.28 mL, 2.21 mmol) was added via syringe. An immediate exothermic ensued with the evolution of methyl chloride. After 15 min the tube was cooled, diluted with CCl_4, and examined by NMR. The exclusive product was the phosphonate **45**, identical with the independently prepared and characterized sample.

2,2-Diphenyl-2-methoxy-2,2-dihydro-5-methyl-1,2-oxaphosphol-4-ene (59). In a dry, nitrogen-purged flask equipped with nitrogen inlet and magnetic stirrer was placed 2 mL of $CDCl_3$ purified by passage through activity 1 neutral alumina. The flask was cooled in an ice bath, and 0.13 mL (0.11 g, 1.54 mmol) of methyl vinyl ketone was added, followed by 0.30 mL (0.33 g, 1.54 mmol) of methyl diphenylphosphinite.[46] After 5 min of mixing, analysis by NMR indicated >90% conversion to oxaphospholene **59:** NMR ($CDCl_3$) δ 8.38–7.35 (10, m, Ph), 4.73 (d of m, 1, J_{PH} = 43 Hz, -CH=), 3.36 (d of d of q, 2, J_{PH} = 17.5, J_{HH} = 2.5, J_{HH} = 2.5 Hz, $-CH_2-$), 2.98 (d, 3, J_{PH} = 10 Hz, $POCH_3$), and 1.83 ppm (broad s, 3, CH_3).

Reaction of 59 with Triethylchlorosilane. To the solution of **59** (1.54 mmol) in $CDCl_3$ prepared above was added 0.52 mL (3.1 mmol) of triethylchlorosilane. An immediate reaction ensued with the production of phosphine oxide **48** which was identical with authentic sample. In addition to **48**, a small amount (ca. 5%) of the corresponding hydrolysis product, 3-oxobutyldiphenylphosphine oxide, was produced.

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