Direct Synthesis of Terminal Olefins from Ketones. Application of (Chloromethyl)trimethylsilane to a Wittig Reaction[1]
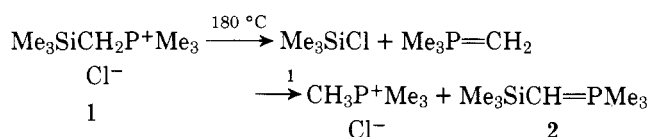
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The reactions of carbonyl compounds with (chloromethyl)trimethylsilane in the presence of triphenylphosphine gave terminal olefins in high yields. In the reactions of carbonyl compounds having α-hydrogen, silyl enol ethers were obtained together with terminal olefins. (Chloromethyl)trimethylsilane reacts with triphenylphosphine followed by elimination of trimethylchlorosilane and methylenetriphenylphosphorane, which converts carbonyl compounds into terminal olefins. Stilbene was also produced in good yield from the reaction of benzaldehyde with (α-bromobenzyl)trimethylsilane.

Several methods for the conversion of carbonyl compounds into terminal olefins have been developed during the past years. One of the most useful syntheses of terminal olefins from carbonyl compounds is the Wittig reaction, in which carbonyl compounds react with phosphonium ylides, giving olefins and phosphine oxide.[2] However, in many cases the Wittig reagents are prepared in an anhydrous solvent under an atmosphere of inert gas, using a base such as phenyllithium or butyllithium. Miller discovered the distillable ylide [(trimethylsilyl)methylene]trimethylphosphorane (2) by a solid state pyrolysis of trimethyl[(trimethylsilyl)methyl]phosphonium chloride (1) under vacuum.[3] The results could be rationalized by a mechanism in which the chloride ion attacks the silicon site in the phosphonium chloride 1, leading to trimethylchlorosilane and methylenetrimethylphosphorane, the latter abstracting a proton from 1 to give ylide 2 and tetramethylphosphonium chloride. The phosphonium salt 1 has been pyrolyzed with acetone to give isobutylene, but in low yield. These results led us to study the reaction of (halomethyl)trimethylsilane and carbonyl compounds in the presence of triphenylphosphine. We wish to report here the direct transformation of carbonyl groups into terminal olefins by use of (halomethyl)trimethylsilane.

$$Me_3SiCH_2P^+Me_3 \xrightarrow{180\,°C} Me_3SiCl + Me_3P{=}CH_2$$
$$Cl^-$$
$$\mathbf{1} \xrightarrow{} CH_3P^+Me_3 + Me_3SiCH{=}PMe_3$$
$$Cl^- \qquad\qquad \mathbf{2}$$

Results and Discussion

When the reaction of benzophenone (1.01 mmol) and (chloromethyl)trimethylsilane (3.06 mmol) in the presence of triphenylphosphine (1.52 mmol) was carried out at 150 °C in a sealed tube, triphenylphosphine oxide and 1,1-diphenylethylene were obtained in 100 and 78% yields, respectively. Formation of trimethylchlorosilane was found by GLC analysis.

$$Me_3SiCH_2Cl + Ph_3P + Ph_2CO$$
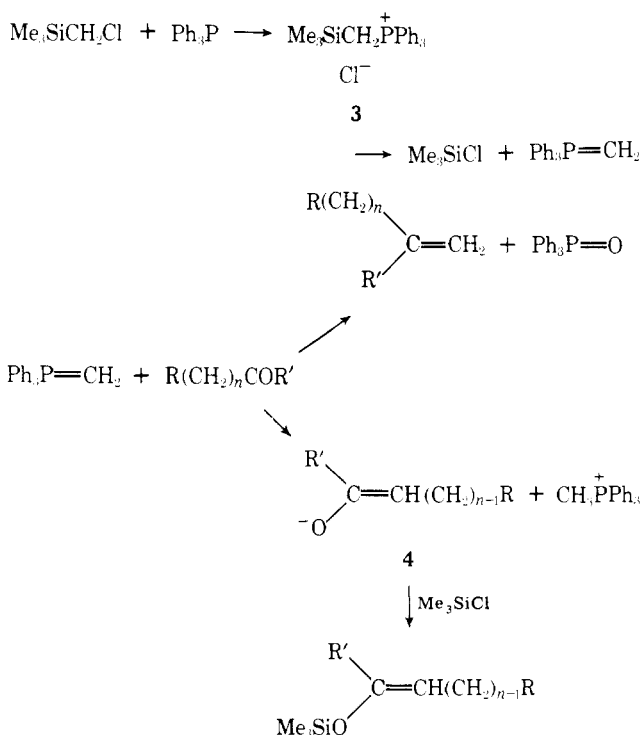$$\xrightarrow{150\,°C} Ph_2C{=}CH_2 + Ph_3P{=}O + Me_3SiCl$$
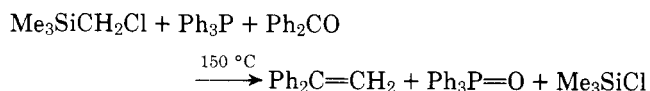
In order to elucidate the best conditions, effects of the reaction temperature and solvents on the yield of diphenylethylene were investigated. The results are summarized in Table I. When the reaction was carried out at above 150 °C, diphenylethylene was formed in quantitative yield, while at 93 °C only a trace of the olefin was obtained even after 1 h and the major part of triphenylphosphine (93%) remained. The failure to produce the olefin at low temperature may arise from insufficient formation of [(trimethylsilyl)methyl]triphenylphosphonium chloride. Furthermore, the solvents were

not significantly favored to give the olefin by similar reasons. The amount of triphenylphosphine also affected the yield of diphenylethylene. As shown in Table II, the olefin was formed quantitatively when a 1.5-mmol amount of triphenylphosphine was applied.

The reactions of (chloromethyl)trimethylsilane with a variety of carbonyl compounds were carried out in the presence of triphenylphosphine, and the corresponding terminal olefins were obtained in good yields (Table III). The methylenation by use of (chloromethyl)trimethylsilane appears to be operationally simpler and cleaner than that of the Wittig reaction by means of a base. However, in the reactions with carbonyl compounds having α-hydrogens, silyl enol ethers were formed together with the expected terminal olefins. This method is suitable only for the ketones having no enolizable α-hydrogens because of competing silyl enol ether formation.

The initial reaction may involve the formation of [(trimethylsilyl)methyl]triphenylphosphonium chloride (3) in the reaction of (chloromethyl)trimethylsilane and triphenylphosphine.[4] The second step may be the cleavage of the silicon–carbon bond of 3 by chloride ion to produce trimethylchlorosilane and methylenetriphenylphosphorane. The latter reacts either with carbonyl to give terminal olefin or with α-hydrogen to produce enolate ion 4,[2] which affords the silyl enol ether by reaction with trimethylchlorosilane. When the re-

$$Me_3SiCH_2Cl + Ph_3P \longrightarrow Me_3SiCH_2\overset{+}{P}Ph_3$$
$$Cl^-$$
$$\mathbf{3}$$
$$\longrightarrow Me_3SiCl + Ph_3P{=}CH_2$$

[structure diagram showing branching reactions producing]

$$\underset{R'}{\overset{R(CH_2)_n}{>}}C{=}CH_2 + Ph_3P{=}O$$

$$Ph_3P{=}CH_2 + R(CH_2)_n COR'$$

$$\underset{{}^-O}{\overset{R'}{>}}C{=}CH(CH_2)_{n-1}R + CH_3\overset{+}{P}Ph_3$$
$$\mathbf{4}$$
$$\downarrow Me_3SiCl$$
$$\underset{Me_3SiO}{\overset{R'}{>}}C{=}CH(CH_2)_{n-1}R$$

Table I. Synthesis of 1,1-Diphenylethylene in the Reaction of (Chloromethyl)trimethylsilane and Benzophenone[a]

conditions			recovered Ph_2CO,[b] %	olefin $Ph_2C=CH_2$,[b] %
temp, °C	time, min	solvent		
176	30		0	100
154	30		0	100
150	10		0	90 (78)[c]
123	30		48	40
123	60		26	71
93	30		96	0
93[d]	60		88	3
123	60	dioxane	100	0
123	60	xylene	92	8
123	60	anisole	75	13
123	60	benzonitrile	80	14
123	60	DMF	75	23

[a] Benzophenone (1 mmol), triphenylphosphine (1.5 mmol), and (chloromethyl)trimethylsilane (3 mmol) were used. [b] Yields were determined by GLC. [c] Parentheses show isolated yield. [d] Unreacted triphenylphosphine (93%) was obtained as methyltriphenylphosphonium iodide on addition of methyl iodide to the reaction mixture.

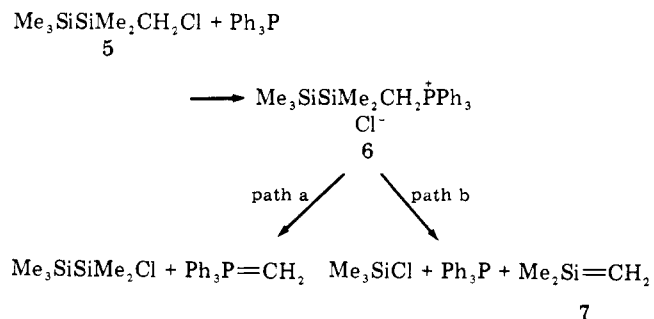### Table II. Effect of Amount of Triphenylphosphine on the Yield[a]

Ph_2CO, mmol	Ph_3P, mmol	recovered Ph_2CO,[b] %	olefin $Ph_2C=CH_2$,[b] %
1.02	0.51	42	36
1.01	1.10	trace	81
1.03	1.57	0	100

[a] The reaction was carried out at 150 °C for 1 h using 3 mmol of (chloromethyl)trimethylsilane. [b] GLC yield.

action of triphenylphosphine and (chloromethyl)trimethylsilane was carried out in the absence of carbonyl compounds, an unidentified brown solid which was not the phosphonium salt 3 was formed. The reaction in the absence of ketones was complicated and did not give any mechanical information. Olefin formation was unsuccessful when the reaction of tri-

phenylphosphine and (chloromethyl)trimethylsilane was carried out with the removal of trimethylchlorosilane and then followed by the addition of ketones.
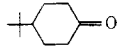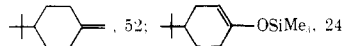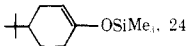
(Chloromethyl)pentamethyldisilane 5 is an interesting compound which can be subject to cleavage either of a silicon-carbon bond (path a) or of a more weak silicon–silicon bond, leading to a dimethylsilene 7[5] (path b). When the re-

$$Me_3SiSiMe_2CH_2Cl + Ph_3P$$
$$\mathbf{5}$$

$$\longrightarrow Me_3SiSiMe_2CH_2\overset{+}{P}Ph_3$$
$$Cl^-$$
$$\mathbf{6}$$

path a / \ path b

$$Me_3SiSiMe_2Cl + Ph_3P=CH_2 \qquad Me_3SiCl + Ph_3P + Me_2Si=CH_2$$
$$\mathbf{7}$$

action of disilane 5 with benzophenone together with triphenylphosphine was carried out at 160 °C for 1 h, diphenylethylene (92%) and triphenylphosphine oxide (96%) were obtained. Pentamethylchlorodisilane was also isolated by preparative GLC, but no trimethylchlorosilane was obtained. The observations show that the more positive silicon in the phosphonium salt 6 was attacked by chloride ion to release methylenetriphenylphosphorane (path a), not dimethylsilene 7 (path b).

Treatment of carbonyl compounds with reagents such as (bromomethyl)trimethylsilane or (iodomethyl)trimethylsilane did not give satisfactory results. A mixture of benzophenone (1.01 mmol), triphenylphosphine (1.51 mmol), and (bromomethyl)trimethylsilane (3.11 mmol) was heated at 150 °C for 30 min. Insoluble material on addition of petroleum ether to the reaction mixture was isolated and found to be [(trimethylsilyl)methyl]triphenylphosphonium bromide.[6,7] The fraction of the petroleum ether contained 18% of diphenylethylene by GLC analysis. On the other hand, the reaction of (iodomethyl)trimethylsilane with benzophenone in the presence of triphenylphosphine under the same conditions gave only [(trimethylsilyl)methyl]triphenylphosphonium iodide,[8] and no diphenylethylene was formed. Unfavorable formation of methylenetriphenylphosphorane in the cases of (bromo- and iodomethyl)trimethylsilanes might be affected

### Table III. Reaction of (Chloromethyl)trimethylsilane with Various Carbonyl Compounds[a]

ketone	registry no.	time, min	recovered ketone,[b] %	product,[b] %	registry no.
$Me_3SiCOPh$	5908-41-8	10	0	$Me_3Si(Ph)C=CH_2$, 100 (70)	1923-01-9
$Et_3SiCOPh$	63935-93-3	9	0	$Et_3Si(Ph)C=CH_2$, 80 (65)	42478-41-1
Me_3CCOPh	938-16-9	10	49	$Me_3C(Ph)C=CH_2$, 41 (24)	5676-29-9
		60	9	62 (57)	
(adamantanone)	700-58-3	60	14	(methyleneadamantane) 82 (52)	875-72-9
PhCOMe	98-86-2	10	38	$Ph(Me)C=CH_2$, 47; $Ph(Me_3SiO)C=CH_2$, 15	98-83-9;
		60	12	57; 24	13735-81-4
$PhCOCH_2CH_3$	93-55-0	60	15	$Ph(Et)C=CH_2$, 49; $Ph(Me_3SiO)C=CHMe$, 32	2039-93-2; 37471-46-8
(4-tert-butylcyclohexanone)	98-53-3	15	29	(alkene) 52; (OSiMe₃ product) 24	13294-73-0; 19980-19-9
		60	0	63; 37	
$PhCH_2CH_2CHO$	104-53-0	60	17	$PhCH_2CH_2CH=CH_2$,[d] 9; $PhCH_2CH=CHOSiMe_3$, 42[c]	

[a] The reaction was carried out at 150 °C without solvent using ketone (1 mmol), triphenylphosphine (1.5 mmol), and (chloromethyl)trimethylsilane (3 mmol). [b] Yields were determined by GLC. Isolated yields are given in parentheses. [c] A mixture of trans (28%) and cis (14%) isomers. [d] Registry no., 768-56-9.

with weak bond formation of silicon–bromine (69 kcal/mol) and silicon–iodine (51 kcal/mol), in contrast with that of silicon–chlorine (86 kcal/mol).

Since fluoride ion is known to have an affinity and cleaves a silicon–carbon bond,[9] the reaction of [(trimethylsilyl)-methyl]triphenylphosphonium iodide with fluoride ion was examined. Benzophenone (0.28 mmol), potassium fluoride (0.39 mmol), and 18-crown-6 (0.08 mmol) were added to a suspension of the phosphonium iodide (0.28 mmol) in dry THF and refluxed for 4 h to yield 7% of diphenylethylene. Addition of tetrabutylammonium fluoride in place of potassium fluoride increased the yield of diphenylethylene to 18%, but the main part was methyltriphenylphosphonium iodide (60%), probably formed by the moisture. Sodium methoxide was also used for the scission of the silicon–carbon bond of the phosphonium iodide and found to give diphenylethylene in 30% yield.

Our studies were extended to the preparation of stilbene using easily available (α-bromobenzyl)trimethylsilane. The reactions of substituted benzaldehydes and (α-bromobenzyl)trimethylsilane were carried out at 170 °C for 1 h. Separation by silica gel chromatography gave *trans*-stilbenes in good yields, and no cis isomer was formed.

Me₃SiCHBrPh + Ph₃P + X—⟨O⟩—CHO

$\xrightarrow{170\ °C}$ X—⟨O⟩—CH=CH—⟨O⟩

X	yield, %
H	59
Me	85
Cl	88
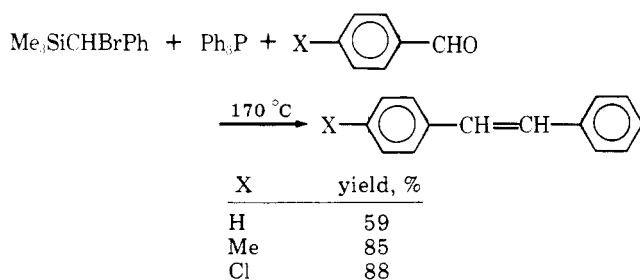
However, the reactions of ketones having α-hydrogens such as acetophenone or cyclohexanone under the above conditions led to the formation of benzyltriphenylphosphonium bromide instead of the expected olefins. Benzylidenetriphenylphosphorane probably abstracts a proton to give the phosphonium bromide instead of undergoing a Wittig reaction by steric hindrance.

Experimental Section

The IR and NMR spectra were recorded on Hitachi 215 and Hitachi R-24A spectrometers, respectively. Analyses were done on an Ohukura gas chromatograph with a 5 mm × 1.5 m stainless column of 15% SF-96 and with a 5 mm × 1 m stainless column of 3% SF-96 on Celite 545. All melting points were uncorrected.

Materials. (Chloromethyl)trimethylsilane,[10] (bromomethyl)trimethylsilane,[11] (iodomethyl)trimethylsilane,[12] (chloromethyl)pentamethyldisilane,[13] and (α-bromobenzyl)trimethylsilane[14] were prepared by known procedures as referenced.

Reaction of Ketone with (Chloromethyl)trimethylsilane in the Presence of Triphenylphosphine. Reactions were normally conducted on a 1-mmol scale of carbonyl compounds in a Pyrex tube as follows. A mixture of ketone (1 mmol), (chloromethyl)trimethylsilane (3 mmol), and triphenylphosphine (1.5 mmol) was heated under the indicated conditions. Yields were obtained relative to the area of a known amount of internal standard by GLC. For isolation of the olefins, petroleum ether was added to the reaction mixture at the completion of the reaction. Triphenylphosphine oxide was filtered off, and then the residue from the petroleum ether solution was chromatographed on silica gel. Products were identified by comparison of NMR and IR spectra with those of authentic samples. α-

(Trimethylsilyl)styrene,[15] 3,3-dimethyl-2-phenyl-1-butene,[16] methyleneadamantane,[17] α-(trimethylsiloxy)styrene,[18] 2-phenyl-1-butene,[19] 1-phenyl-1-(trimethylsiloxy)-1-propene,[20] 4-methylene-*tert*-butylcyclohexane,[21] 4-*tert*-butyl-1-(trimethylsiloxy)-cyclohexene,[18] 4-phenyl-1-butene,[22] and 3-phenyl-1-(trimethylsiloxy)-1-propene[23] are known compounds. α-(Triethylsilyl)styrene was identified by its NMR, IR, mass, and elemental analyses: NMR (CCl₄) δ 0.2–1.1 (15 H, m, SiEt), 5.53 (1 H, d, *J* = 3 Hz, C=CH), 5.80 (1 H, d, *J* = 3 Hz, C=CH), and 6.8–7.3 (5 H, m, ArH); IR (neat) 1005 cm⁻¹ (C=CH₂); mass spectrum (at 20 eV), *m/e* (relative intensity) 218 (M⁺, 7), 191 (13), 190 (63), 189 (88), 162 (14), 161 (100), 135 (16), 133 (40), and 87 (28). Anal. Calcd for C₁₄H₂₂Si: C, 77.0; H, 10.2. Found: C, 77.0; H, 9.7.

Reaction of Benzophenone with (Chloromethyl)pentamethyldisilane in the Presence of Triphenylphosphine. The reaction of benzophenone (1.00 mmol) with (chloromethyl)pentamethyldisilane (3.02 mmol) in the presence of triphenylphosphine (1.50 mmol) was also carried out in a similar manner as described above to give diphenylethylene (92%) and triphenylphosphine oxide (96%).

Reaction of Benzaldehyde with (α-Bromobenzyl)trimethylsilane in the Presence of Triphenylphosphine. A mixture of benzaldehyde (2.12 mmol), (α-bromobenzyl)trimethylsilane (5.19 mmol), and triphenylphosphine (2.97 mmol) was heated in a sealed tube at 170 °C for 1 h. *trans*-Stilbene, mp 123–124 °C (lit.[22] mp 124 °C), was isolated by silica gel chromatography in 59% yield. The reactions of *p*-methylbenzaldehyde or *p*-chlorobenzaldehyde with (α-bromobenzyl)trimethylsilane were carried out in the same manner to yield *trans*-4-methylstilbene (85%), mp 118–119 °C (lit.[24] mp 119 °C), and *trans*-4-chlorostilbene (88%), mp 128.5–129.5 °C (lit.[24] mp 129 °C), respectively.

Registry No.—*cis*-3-Phenyl-1-(trimethylsiloxy)-1-propene, 51425-56-0; *trans*-3-phenyl-1-(trimethylsiloxy)-1-propene, 51425-55-9; (chloromethyl)trimethylsilane, 2344-80-1; (bromomethyl)trimethylsilane, 18243-41-9; (iodomethyl)trimethylsilane, 4206-67-1; (chloromethyl)pentamethyldisilane, 5181-46-4; (2-bromobenzyl)-trimethylsilane, 17903-41-2; benzophenone, 119-61-9; 1,1-diphenylethylene, 530-48-3; benzaldehyde, 100-52-7; *trans*-stilbene, 103-30-0; *p*-methylbenzaldehyde, 104-87-0; *p*-chlorobenzaldehyde, 104-88-1; *trans*-4-methylstilbene, 1860-17-9; *trans*-4-chlorostilbene, 1657-50-7.

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