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THE WITTIG SYNTHESIS OF ALLYLIC ORGANOSILICON COMPOUNDS *

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Summary

The reactions of β-silylalkylidenetriphenylphosphoranes (prepared by the action of alkylidenetriphenylphosphoranes on iodomethylsilicon compounds, followed by deprotonation of the resulting β-silylalkyltriphenylphosphonium iodides) with aldehydes and ketones provide a useful route to allylic silicon compounds. The β-silyl Wittig reagents prepared and utilized in this study include $Ph_3P{=}CHCH_2SiMe_3$, $Ph_3P{=}C(CH_3)CH_2SiMe_3$, $Ph_3P{=}C(C_6H_5)CH_2SiMe_3$, $Ph_3P{=}CHCH_2SiMe_2H$, $Ph_3P{=}CHCH_2SiMe_2OSiMe_3$ and $Ph_3P{=}CHCH_2SiMe(OSiMe_3)_2$.

Introduction

Allylic silicon compounds are of current interest since they have been found to be useful reagents in organic synthesis [2]. Their synthesis may be effected by organolithium and organomagnesium routes, as well as by 1,4-addition of silicon hydrides to 1,3-dienes and by the $Et_3N/CuCl$ induced condensation of trichlorosilane with allylic halides [2]. These procedures all involve silicon—carbon bond forming reactions. We have developed an alternative allylsilane synthesis which is based on the C=C bond forming Wittig reaction. Halomethyl- and α-haloalkylsilanes are easily prepared [3]. Various chloromethylsilicon compounds are commercially available [4], and these may be converted to the more reactive iodomethylsilanes by the action of sodium iodide in anhydrous acetone [5]. In view of the high reactivity toward nucleophilic reagents of the halomethylsilanes in general [3], they would be expected to react readily with phosphorus ylides to form β-silylethylphosphonium halides, e.g., eq. 1. Deprotona-

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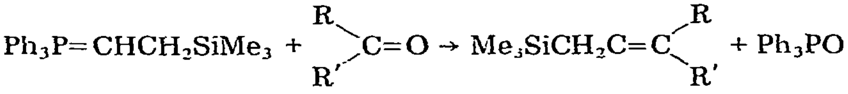
tion of the latter then should give β-silyl ylides whose reactions with aldehydes

$$Ph_3P{=}CH_2 + ICH_2SiMe_3 \rightarrow [Ph_3PCH_2CH_2SiMe_3]^+I^- \qquad (1)$$

and ketones would produce allylic silanes (eq. 2, 3). The reaction sequence shown in eq. 1, 2 and 3 has been found to proceed readily and we present here

$$[Ph_3PCH_2CH_2SiMe_3]^+I^- \xrightarrow{base} Ph_3P{=}CHCH_2SiMe_3 \qquad (2)$$



$$Ph_3P{=}CHCH_2SiMe_3 + R(R')C{=}O \rightarrow Me_3SiCH_2C{=}C(R)(R') + Ph_3PO \qquad (3)$$

the details of these and related reactions.

Results and discussion

The addition of a solution of methylenetriphenylphosphorane (salt-free, prepared by deprotonation of methyltriphenylphosphonium bromide with sodium amide in liquid ammonia) in diethyl ether to a cold (0°C) ether solution of iodomethyltrimethylsilane resulted in the slow precipitation of a solid. After the reaction mixture had been stirred at room temperature for 15 h, it was light amber in color. Filtration gave the desired β-trimethylsilylethyltriphenylphosphonium iodide, $[Ph_3PCH_2CH_2SiMe_3]^+I^-$, in 88% yield. An analytically pure sample was obtained by recrystallization from water.

Similar reactions of methylenetriphenylphosphorane with Me_2HSiCH_2I, $Me_3SiOSiMe_2CH_2I$ and $(Me_3SiO)_2MeSiCH_2I$ gave the expected phosphonium halides, $[Ph_3PCH_2CH_2SiMe_2H]^+I^-$, $[Ph_3PCH_2CH_2SiMe_2OSiMe_3]^+I^-$ and $[Ph_3PCH_2CH_2SiMe(OSiMe_3)_2]^+I^-$, respectively. The addition of ethylidenetriphenylphosphorane to iodomethyltrimethylsilane resulted in formation of $[Ph_3PCH(CH_3)CH_2SiMe_3]^+I^-$ and a similar reaction with benzylidenetriphenylphosphorane produced $[Ph_3PCH(C_6H_5)CH_2SiMe_3]^+I^-$.

Thus β-silylalkylphosphonium salts can be prepared, in most cases in good yield, from readily accessible starting materials. In some of these syntheses methyltriphenylphosphonium iodide is formed as a by-product. This impurity is readily removed by fractional crystallization. Alternatively, it need not be removed from the crude phosphonium halide since the olefin obtained from the Wittig reaction of its derived ylide is sufficiently low boiling (relative to the allylic silane prepared, as in eq. 3) so that it causes no problems in product purification. The formation of $[Ph_3PCH_3]^+I^-$ as a by-product was a particularly serious problem in the case of the $Ph_3P{=}CH_2/ICH_2SiMe(OSiMe_3)_2$ reaction.

It is not wholly clear how the $[Ph_3PCH_3]^+I^-$ impurity is formed. Since a reaction of $Ph_3P{=}CH_2$, which is a strong base as well as an effective nucleophile, is involved, it could be formed in a deprotonation reaction with either Me_3SiCH_2I or the product, $[Ph_3PCH_2CH_2SiMe_3]^+I^-$, in the case of the $Ph_3P{=}CH_2/Me_3SiCH_2I$ reaction. Deprotonation of higher alkyltriphenylphosphonium salts by $Ph_3P{=}CH_2$ generally is an unfavorable reaction [6]. For instance, for the equilibrium shown in eq. 4, the constant, K_{eq}, is ~0.05. α-Silyl substituents strongly favor formation of the ylide; thus the reaction shown in eq. 5 proceeds far to the right [7].

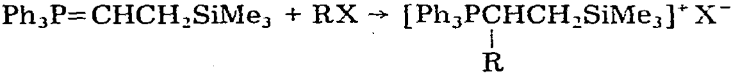
$$Ph_3P{=}CH_2 + [Ph_3PCH_2CH_3]^+Br^-(s) \xrightleftharpoons{Et_2O} Ph_3P{=}CHCH_3 + [Ph_3PCH_3]^+Br^-(s) \quad (4)$$

$$[Ph_3PCH_2SiMe_3]^+Br^- + Ph_3P{=}CH_2 \rightarrow Ph_3P{=}CHSiMe_3 + [Ph_3PCH_3]^+Br^- \quad (5)$$

This, however, appears to be a specific α-effect involving orbital interaction between the silicon atom and the α carbanionic center. A control experiment in which an ether solution of methylenetriphenylphosphorane was added to an ether slurry of $[Ph_3PCH_2CH_2SiMe_3]^+I^-$ did result in color changes of the solution from the yellow of the original ylide to orange to orange-red. However, when cyclohexanone was added to this mixture after it had been stirred at room temperature overnight, only methylenecyclohexane was formed (66% yield). No product derived from the β-silyl ylide, 2-cyclohexylideneethyltrimethylsilane, was present. In view of this result, it seems likely that the methyltriphenylphosphonium iodide by-product arises from deprotonation of the iodomethylsilicon compound.

The β-silylalkyltriphenylphosphonium iodides prepared could be converted to the respective ylides by reaction with phenyl- or methyllithium or lithium diisopropylamide in diethyl ether, THF or diethyl ether/THF at 0°C. In contrast to such reactions of β-trimethylstannylethyltriphenylphosphonium iodide with phenyllithium, there was no attack by the lithium reagent at silicon, hence no Si—C cleavage. The ylide $Ph_3P{=}CHCH_2SiMe_3$ reacted readily with aldehydes and some ketones to give the respective allylic silanes. The α-substituted ylide, $Ph_3P{=}C(CH_3)CH_2SiMe_3$, reacted with propionaldehyde and benzaldehyde to give the expected Wittig product, but it reacted with cyclohexanone to regenerate the phosphonium salt, presumably by way of proton abstraction from the ketone. Such behavior was encountered in the reaction of $Ph_3P{=}C(C_6H_5)CH_2SiMe_3$ even with propionaldehyde. Thus there appears to be a limitation to the applicability of α-substituted ylides of type $Ph_3P{=}C(R)CH_2SiMe_3$ in Wittig allylsilane synthesis due to the steric hindrance to nucleophilic attack at a C=O function caused by the presence of another substituent in addition to the bulky "siliconeopentyl" group on the ylide carbon atom. Such steric hindrance is observed to a lesser extent even with $Ph_3P{=}CHCH_2SiMe_3$ in its reaction with 3-pentanone. Under conditions used in the reactions of this ylide with the less hindered *n*-heptaldehyde and cyclohexanone, which gave good Wittig product yields ($Me_3SiCH_2CH{=}CHC_6H_{13}\text{-}n$, 71%; $Me_3SiCH_2CH{=}C(CH_2)_5$-cyclo, 85%), this ylide reacted with $Et_2C{=}O$ to give $Me_3SiCH_2CH{=}CEt_2$ in only 18% yield. More forcing conditions (long reflux in toluene solution) improved the yield to 38%. Of special interest in this connection is the dimethylsilyl-substituted ylide, $Ph_3P{=}CHCH_2SiMe_2H$. This ylide, with its less bulky Me_2HSi substituent (compared to Me_3Si), reacted readily with $Et_2C{=}O$ at room temperature to give $Me_2HSiCH_2CH{=}CEt_2$ in 55% yield. Thus this ylide, rather than $Ph_3P{=}CHCH_2SiMe_3$, is applicable to the synthesis of allylic silanes from hindered ketones.

Another potential route to β-silylalkyltriphenylphosphonium halides with α-substituents is shown in eq. 6. Although no such syntheses were carried out,



$$Ph_3P{=}CHCH_2SiMe_3 + RX \rightarrow [Ph_3P\underset{R}{\underset{|}{C}}HCH_2SiMe_3]^+X^- \quad (6)$$

such a reaction of $Ph_3P{=}CHCH_2SnMe_3$ with iodomethane gave $[Ph_3PCH(CH_3)CH_2SnMe_3]^+I^-$ in good yield [8]. More highly substituted β-silyl phosphonium salts of type $[Ph_3PCH_2CH(R')SiMe_3]^+X^-$ and $[Ph_3PCH(R)CH(R')SiMe_3]^+X^-$ should be accessible by reactions of $Ph_3P{=}CH_2$ and of substituted methylenetriphenylphosphoranes, $Ph_3P{=}CHR$, with α-haloalkyltrimethylsilanes. These, on reaction with suitable carbonyl compounds, would, in principle, give substituted allylic silanes of type $Me_3SiCH(R')CH{=}CR''R'''$, but difficulties due to steric factors may be expected, thus limiting their scope of applicability.

The siloxane-substituted ylides, $Ph_3P{=}CHCH_2SiMe_2OSiMe_3$ and $Ph_3P{=}CHCH_2SiMe(OSiMe_3)_2$ are of some interest since they provide an entry to allylic siloxane polymers.

Although the present study was of somewhat limited scope, it is clear that the Wittig reaction of β-silylalkylidenetriphenylphosphoranes can find broad application in the synthesis of allylic silicon compounds. Steric factors introduce some limitations, but the replacement of the usual trimethylsilyl function by the readily accessible dimethylsilyl (Me_2HSi) group provides the remedy for at least some of these steric problems.

These Wittig syntheses of allylic silanes as carried out under the conditions described are not stereoselective. In those reactions of $Ph_3P{=}CHCH_2SiMe_3$ and $Ph_3P{=}C(CH_3)CH_2SiMe_3$ with aldehydes the products were mixtures of isomers. Procedures for increasing the stereoselectivity of the Wittig synthesis of olefins are known, but if the *trans* isomers of $Me_3SiCH_2CH{=}CHR$ or the *Z* isomers of $Me_3SiCH_2C(CH_3){=}CHR$ are required, consideration should be given to the easily effected procedure shown in eq. 7, 8 and 9. β-Trimethylstannyl-substituted

$$Ph_3P{=}CRCH_2SnMe_3 + R'CH{=}O \rightarrow Me_3SnCH_2C(R){=}CHR' + Ph_3PO \qquad (7)$$

(R = H or CH_3)

$$Me_3SnCH_2C(R){=}CHR' + MeLi \xrightarrow{THF} Li(CH_2C(R)CHR') + Me_4Sn \qquad (8)$$

$$Li(CH_2C(R)CHR') + Me_3SiCl \rightarrow Me_3SiCH_2C(R){=}CHR' + LiCl \qquad (9)$$

alkyltriphenylphosphonium iodides are readily prepared and converted to the respective ylides. These react with aldehydes in good yield to give allylic tin compounds [8] and the latter react readily with methyllithium in THF to produce allylic lithium reagents which react with trimethylchlorosilane to give allylic silanes in high yield [9]. In examples where R = H, and R′ = *n*-hexyl and phenyl, and R = Me and R′ = ethyl, the stereoselectivity of allylsilane formation was high with the *trans* and the *Z* isomer being highly favored.

The utilization of β-silyl ylides in the synthesis of 3,3-difluoroallylsilicon compounds will be dealt with in a subsequent paper [10].

Experimental

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of dry argon or nitrogen. All solvents were rigorously dried, diethyl ether by distillation from lithium aluminum hydride, tetrahydrofuran (THF) from sodium benzophenone ketyl.

Infrared spectra were recorded using a Perkin Elmer 457A grating infrared spectrophotometer, proton NMR spectra using a Varian Associates T60 spectrometer. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Internal standards used were tetramethylsilane, chloroform and dichloromethane. Gas-liquid chromatography (GLC) was used in product analysis, yield determinations and for isolation of pure product samples for analysis and spectroscopy.

Starting materials

Iodomethylsilicon compounds. Me_3SiCH_2I and the other iodomethylsilicon compounds were prepared from the respective chloromethylsilane and anhydrous sodium iodide in acetone [5]. The preparation of $ICH_2SiMe(OSiMe_3)_2$ was complicated by the formation of substantial quantities of $[ICH_2SiMe(OSiMe_3)]_2O$ during the course of the work-up. $ICH_2SiMe(OSiMe_3)_2$, n_D^{25} 1.4391. (Found: C, 26.60, H, 6.35. $C_8H_{23}IO_2Si_3$ calcd.: C, 26.51; H, 6.40). NMR ($CDCl_3/CHCl_3$): singlets at δ 0.14 (18H), 0.24 (3H) and 1.89 (2H) ppm. $[ICH_2SiMe(OSiMe_3)]_2O$, n_D^{25} 1.4793. NMR ($CDCl_3/CHCl_3$): singlets at δ 0.20 (18H), 0.35 (6H) and 2.08 (4H) ppm. The yields of these products in a reaction in which the reaction mixture simply was filtered and distilled were 39 and 24%, respectively. A much better yield (74%) of the desired product was obtained in a reaction in which the organic layer was washed with water to remove inorganic salts before distillation.

Salt-free methylenetriphenylphosphorane was prepared from methyltriphenylphosphonium bromide and sodium amide by the method of Bestmann [11]. Salt-free ethylidenetriphenylphosphorane was prepared by the same procedure. Benzylidenetriphenylphosphorane was prepared by the action of $(Me_3Si)_2NNa$ on $[Ph_3PCH_2Ph]^+Br^-$ [12].

Preparation of β-silyl-substituted phosphonium iodides

$[Ph_3PCH_2CH_2SiMe_3]^+I^-$. A solution of 0.10 mol of salt-free methylenetriphenylphosphorane in 400 ml of diethyl ether was charged into the dropping funnel of a reaction vessel (one-liter three-necked, round-bottomed flask equipped with a mechanical stirrer, a dropping funnel and a nitrogen inlet tube) which contained 24.0 g (0.11 mol) of iodomethyltrimethylsilane [5a] in 200 ml of dry diethyl ether, and was cooled to 0°C. The ylide solution was added to the iodo compound dropwise over a period of 1 h. The phosphonium iodide precipitated slowly during the course of the addition. Upon completion of the addition an orange slurry was present. The reaction mixture was stirred at room temperature under nitrogen for 15 h; at the end of this time a light amber slurry was present. The mixture was filtered and the residue washed with 500 ml of diethyl ether and dried at reduced pressure (room temperature) to give 42.95 g (88%) of $[Ph_3PCH_2CH_2SiMe_3]^+I^-$. An analytical sample, m.p. 163—164.5°C, was obtained by recrystallization from water. The sample was dried over P_2O_5 (110°C/0.02 mmHg) for 15 h. (Found: C, 56.02; H, 5.81. $C_{23}H_{28}IPSi$ calcd.: C, 56.33; H, 5.75). NMR ($CDCl_3/CH_2Cl_2$): δ 0.08 (s, 9H, Me_3Si), 0.45—0.91 (complex m, 2H, $SiCH_2$), 3.08—3.57 (complex m, 2H, PCH_2) and 7.55—7.93 ppm (m, 15H). The IR spectrum ($CHCl_3$) showed the characteristic Me_3Si absorptions at 1255 and 860/845 cm^{-1}.

This reaction was carried out on larger scale (up to 0.45 mol) with good results. In some cases, NMR examination of the crude product showed the presence of small amounts (up to 6%) of $[Ph_3PCH_3]^+I^-$ impurity. This by-product is minimized by carrying out the reaction at 0°C rather than at room temperature.

$[Ph_3PCH(CH_3)CH_2SiMe_3]^+I^-$. The same procedure was used in the reaction of 35.8 mmol of salt-free $Ph_3P{=}CHCH_3$ in 250 ml of diethyl ether with 40 mmol of Me_3SiCH_2I in 200 ml of diethyl ether. The reaction proceeded only slowly; a reaction time of 20 h at room temperature gave an amber slurry. Filtration (ether wash) gave 16.0 g (89%) of product. A sample was recrystallized from water and dried over P_2O_5 at 110° in vacuo, m.p. 175—176° (dec.). (Found: C, 56.62; H, 5.92. $C_{24}H_{30}IPSi$ calcd.: C, 57.14; H, 5.99). NMR ($CDCl_3/CHCl_3$): δ 0.07 (s, 9H, Me_3Si), 0.14—0.87 (m, 2H, $SiCH_2$), 1.24 (q, $^3J(H{-}H)$ 7.0 Hz, $^2J(P{-}H)$ 20 Hz, 3H, $PCHCH_3$), 4.07—4.57 (m, 1H, P—CH) and 7.67—7.96 ppm (m, 15H). When this reaction was repeated with a reaction time of 36 h, a colorless solution and a white solid resulted. The product was isolated in 87% yield.

$[Ph_3PCH_2CH_2SiMe_2H]^+I^-$. The reaction was carried out using 100 mmol of $Ph_3P{=}CH_2$ in 435 ml of diethyl ether and 13 ml (100 mmol) of Me_2HSiCH_2I in 200 ml of diethyl ether (addition at 0°C). During the course of the addition the solution turned red and a white precipitate formed. After it had been stirred at room temperature overnight, the reaction mixture consisted of a white solid and a colorless solution. The former was filtered (ether wash) to give 45.7 g (93%) of product, 94% pure by NMR, m.p. 106—109°C. A sample was recrystallized from ethyl acetate/hexane to give an analytically pure product, m.p. 123—124°C. (Found: C, 55.27; H, 5.40. $C_{22}H_{26}IPSi$ calcd.: C, 55.46; H, 5.50). NMR ($CHCl_3$): δ 0.20 (d, J 4 Hz, 6H, Me_2Si), 0.60—1.00 (m, 2H, $SiCH_2$), 1.64—1.70 (m, 1H, SiH), 3.20—4.20 (m, 2H, PCH_2) and 7.64—7.98 ppm (m, 15H). The infrared spectrum ($CHCl_3$) showed ν (Si—H) at 2120 cm^{-1}.

$[Ph_3PCH_2CH_2SiMe_2OSiMe_3]^+I^-$. A solution of 8.8 mmol of salt-free $Ph_3P{=}CH_2$ in 20.5 ml of diethyl ether was added to 2.53 g (8.8 mmol) of $Me_3SiOSiMe_2CH_2I$ in 50 ml of diethyl ether at 0°C using the usual procedure. A red solution containing a large amount of fine white solid was produced. This mixture was stirred at room temperature for 20 h. Subsequently, the white solid was filtered, washed with ether and dried. NMR analysis indicated that a mixture containing 93% of the desired phosphonium salt and 7% of $[Ph_3PCH_3]^+I^-$ was present. A yield of 3.10 g (62%) of this material, m.p. 128—130°C, was obtained. Recrystallization of a sample from acetone/diethyl ether followed by drying at 100°C at 0.5 mmHg gave pure product, m.p. 130—131°C. (Found: C, 53.14; H, 6.02. $C_{25}H_{34}OIPSi_2$ calcd.: C, 53.18; H, 6.07). NMR ($CDCl_3/CHCl_3$): δ 0.00 (s, 9H, Me_3Si), 0.20 (s, 6H, Me_2Si), 0.40—1.00 (m, 2H, $SiCH_2$), 3.00—3.72 (m, 2H, PCH_2) and 7.28—7.59 ppm (m, 15H).

$[Ph_3PCH_2CH_2SiMe(OSiMe_3)_2]^+I^-$. Using the procedure described above, a solution of 97.2 mmol of $Ph_3P{=}CH_2$ in 270 ml of diethyl ether was added, at 0°C, to 36.4 g (100.6 mmol) of $ICH_2SiMe(OSiMe_3)_2$ in 250 ml of diethyl ether. White solid began to form immediately upon addition of the ylide, but the solution color remained yellow. The ylide solution was added over a period of 3 h, at the end of this time, the reaction mixture was red in color and contained a large quantity of fine white solid. The mixture was stirred overnight. The solid was filtered, washed with ether and dried to give 26.95 g of material whose NMR spectrum indicated the presence of a mixture of the desired phosphonium iodide contaminated with about 15% of methyltriphenylphosphonium iodide.

Another reaction was carried out in which the ether solvent of the $Ph_3P=CH_2$ was replaced by hexane. An equimolar quantity of $ICH_2SiMe(OSiMe_3)_2$ was added at 0°C to give ultimately an orange solution containing a light orange powder. After the mixture had been stirred overnight, it was filtered, washed with hexane and dried. The product, obtained in much better yield by this procedure (88% vs. 42% in the first experiment) contained (by NMR) about 30% (molar basis) of $[Ph_3PCH_3]^+I^-$.

It was found that methyltriphenylphosphonium iodide could be separated by dissolving the mixture in ethanol/diethyl ether. The impurity crystallized readily and was removed and the desired phosphonium iodide remained in solution. It could be recovered by evaporation of the solvent; a colorless oil was obtained which slowly crystallized to a waxy solid. NMR ($CDCl_3/CH_2Cl_2$): δ 0.08 (s, 18H, Me_3Si), 0.26 (s, 3H, $SiCH_3$), 0.43—0.95 (complex m, 2H, $SiCH_2$), 3.06—3.60 (complex m, 2H, PCH_2) and 7.61—8.03 ppm (m, 15H).

Wittig reactions with β-silyl-substituted phosphorus ylides (Table 1)

$Ph_3P=CHCH_2SiMe_3$

(a) With n-heptaldehyde. A 200 ml, three-necked, round-bottomed flask equipped with a mechanical stirrer, a condenser topped with an argon inlet tube and a no-air stopper was flame-dried, flushed with argon and charged with 9.81 g (20 mmol) of $[Ph_3PCH_2CH_2SiMe_3]^+I^-$ and 80 ml of THF. The slurry was cooled to 0°C and subsequently 21.2 ml of 1*M* phenyllithium in diethyl ether (21 mmol) was added dropwise with stirring. The mixture immediately turned red. After the mixture had been stirred at room temperature for 1 h, a homogeneous red solution was formed. n-Heptaldehyde (3.0 ml, ca. 22 mmol) was added dropwise and the reaction mixture was heated at reflux for 15 h. During this time the red ylide color was discharged. Trap-to-trap distillation in vacuo of volatiles into a receiver at −78°C was followed by GLC analysis (10% DC 200 on Chromosorb P, 160°C) of the distillate. It was established that 2-nonenyltrimethylsilane, $Me_3SiCH_2C=CHC_6H_{13}\text{-}n$, had been formed in 71% yield. An approximately 1/1.70 ratio of *cis* and *trans* isomers was present: n_D^{25} 1.4386. (Found: C, 72.75; H, 13.26. $C_{12}H_{26}Si$ calcd.: C, 72.63; H, 13.21). NMR (CCl_4/CH_2Cl_2): δ 0.02 and 0.05 (2s, 9H total, 1/1.7 ratio, $SiMe_3$), 0.67—1.47 (complex m, 13H, C_6H_{13}), 1.57—2.13 (m, 2H, $SiCH_2$) and 5.08—5.47 ppm (m, 2H, CH=CH). By analogy with the *cis* and *trans* isomers of crotyltrimethylsilane and the corresponding stannane [13] the higher field resonance of lower intensity may be attributed to the *cis* isomer and the lower field Me_3Si resonance to the *trans* isomer. A band of medium intensity at 965 cm^{-1} in the IR spectrum of the isomer mixture confirmed the presence of the *trans* isomer [14].

(b) With 3-pentanone. To a slurry of 5.41 g (11.03 mmol) of the phosphonium iodide in 40 ml of THF at 0°C was added 11.6 mmol of methyllithium in 5.8 ml of diethyl ether. The resulting yilde solution was stirred under nitrogen at room temperature for 1 h and then 2 ml (ca. 19 mmol) of 3-pentanone was added. The ylide color was discharged only very slowly. The reaction mixture

TABLE 1

REACTIONS OF β-SILYL-SUBSTITUTED ALKYLIDENETRIPHENYLPHOSPHORANES WITH ALDEHYDES AND KETONES

Alkylidenephosphorane	Generating base (solvent)	Carbonyl compound	Reaction time (temperature)	Product (% yield)
$Ph_3P{=}CHCH_2SiMe_3$	PhLi (Et_2O/THF)	$n\text{-}C_6H_{13}CHO$	15 h (reflux)	$Me_3SiCH_2CH{=}CHC_6H_{13}\text{-}n$ (71) [a]
	MeLi (Et_2O/THF)	$C_6H_{10}O$ [g]	12 h (reflux)	$Me_3SiCH_2CH{=}C(CH_2)_5$-cyclo (85) [h]
	MeLi (Et_2O/THF)	C_6H_5CHO	15 h (reflux)	$Me_3SiCH_2CH{=}CHC_6H_5$ (63) [b,f]
	MeLi (Et_2O)	$(CF_3)_2CO$	2.5 days (room temperature) [b]	$Me_3SiCH_2CH{=}C(CF_3)_2$ (43) [c]
	MeLi (Et_2O/THF)	Et_2CO	6 h (reflux) 15 h (reflux) 40 h (100°C)	$Me_3SiCH_2CH{=}CEt_2$ (18) (27) (38)
$Ph_3P{=}C(CH_3)CH_2SiMe_3$	i-Pr_2NLi (THF)	C_2H_5CHO	15 h (reflux)	$Me_3SiCH_2C(CH_3){=}CHC_2H_5$ (68) [d]
	i-Pr_2NLi (THF)	C_6H_5CHO	15 h (reflux)	$Me_3SiCH_2C(CH_3){=}CHC_6H_5$ (72) [e]
	MeLi (Et	C_2H_5CHO	3 h (reflux) + 15 h (room temp.)	$Me_3SiCH_2C(CH_3){=}CHC_2H_5$ (74)
$Ph_3P{=}CHCH_2SiMe_2H$	MeLi (Et_2O)	$C_6H_{10}O$ [g]	1 h (room temp.)	$Me_2HSiCH_2CH{=}C(CH_2)_5$-cyclo (71) [h]
	MeLi (Et_2O)	Et_2CO	1 h (room temp.)	$Me_2HSiCH_2CH{=}CEt_2$ (55)
$Ph_3P{=}CHCH_2SiMe_2OSiMe_3$	i-Pr_2NLi (Et_2O)	$C_6H_{10}O$ [g]	4 h (reflux) + 17 h (room temp.)	$Me_3SiOSiMe_2CH_2CH{=}C(CH_2)_5$-cyclo (50) [h]

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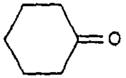
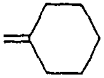
[a] 1/1.7 Ratio of *cis* and *trans* isomers. [b] 40% Yield of *trans* isomer, 23% of *cis*. [c] A −78°C cold condenser was used since $(CF_3)_2CO$ is a gas. [d] 1/1.2 isomer mixture. [e] 1/1.1 isomer mixture. [f] A 10% yield of $PhCH(OSiMe_3)CH{=}CH_2$ also was obtained. [g] $C_6H_{10}O$ =  . [h] = $C(CH_2)_5$-cyclo =  .

was stirred and heated at reflux for 6 h and subsequently was trap-to-trap distilled in vacuo into a receiver at —78° C. The distillate was analyzed by GLC. The presence of 3-ethyl-2-pentenyltrimethylsilane, $Me_3SiCH_2CH{=}CEt_2$, was established. A yield of 2.01 mmol (18%) was obtained. A similar reaction with a longer reaction time of 15 h at reflux gave this product in 27% yield. A third reaction was carried out as above. After the 15 h reflux period the reaction mixture was diluted with 40 ml of toluene and THF was stripped off at atmospheric pressure until the distillation haed temperature reached 100°C. The mixture then was heated at reflux for 40 h. A 38% yield of $Me_3SiCH_2CH{=}CEt_2$ was realized.

$Ph_3P{=}C(CH_3)CH_2SiMe_3$

(a) With benzaldehyde. To an ice-cold solution of 7.3 mmol of lithium diisopropylamide in 35 ml of THF was added 3.50 g (6.94 mmol) of $[Ph_3PCH(CH_3)CH_2SiMe_3]^+ I^-$. The resulting red-brown ylide solution was stirred for 2 h at room temperature and then 0.75 ml (ca. 7.3 mmol) of benzaldehyde was added. The reaction mixture was heated at reflux for 15 h. Trap-to-trap distillation in vacuo gave a distillate whose analysis by GLC (10% DC 200 on Chromosorb P, 180°C) indicated the presence of 2.62 and 2.39 mmol, respectively, (72% total yield) of the isomers of $Me_3SiCH_2C(CH_3){=}CHC_6H_5$.

(b) With cyclohexanone. A solution of $Ph_3P{=}C(CH_3)CH_2SiMe_3$ (from 10.0 mmol of the phosphonium iodide and lithium diisopropylamide) in 25 ml of THF was treated, at room temperature, with 1.2 ml (ca. 12 mmol) of cyclohexanone. The mixture became colorless and a white solid precipitated during the course of 15 min. The reaction mixture was heated at reflux for 15 h and then was trap-to-trap distilled in vacuo. GLC analysis showed that no higher boiling products were present. The pot residue from the distillation afforded 4.63 g (92%) of a solid whose NMR spectrum matched that of the starting phosphonium iodide.

$Ph_3P{=}CHCH_2SiMe_2H$

(a) With cyclohexanone. To a slurry of 2.38 g (5.0 mmol) of $[Ph_3PCH_2CH_2SiMe_2H]^+I^-$ in 20 ml of diethyl ether which was cooled in an ice bath was added dropwise (under argon) 5 mmol of methyllithium in 3.5 ml of diethyl ether. The resulting reddish-brown solution was stirred at room temperature for 1 h and then 1 ml (ca. 10 mmol) of cyclohexanone was added dropwise at 0°C. After it had been stirred for 1 h, the reaction mixture was colorless and contained a large amount of white solid. Trap-to-trap distillation in vacuo into a receiver at —75°C was followed by GLC analysis of the distillate (SE-30 at 140°C). The expected product, cyclo-$(CH_2)_5C{=}CHCH_2SiMe_2H$, was obtained in 71% yield.

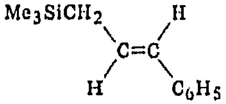
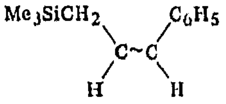
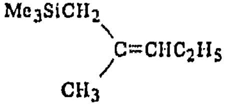
(b) With 3-pentanone. The ylide was prepared from 2.7 mmol of the phosphonium iodide and 2.7 mmol of methyllithium in diethyl ether. 3-Pentanone (0.26 g, 3 mmol) was added at room temperature and then the mixture was stirred for 1 h. Trap-to-trap distillation and GLC analysis of the distillate followed. A 55% yield of $Et_2C{=}CHCH_2SiMe_2H$ was obtained.

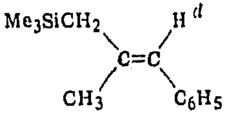
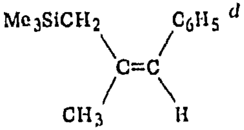
$Ph_3P{=}CHCH_2SiMe_2OSiMe_3$

(a) With cyclohexanone. A solution of lithium diisopropylamide was prepared

TABLE 2

NEW COMPOUNDS

Compounds	n_D^{25}	Analysis (%) Found (calcd.)		^{1}H NMR (in CCl$_4$), δ (ppm)
		C	H	
Me$_3$SiCH$_2$CH=CHC$_6$H$_{13}$-*n* (1/1.7 ratio of *cis* and *trans* isomers)	1.4386 ^{a}	72.75 ^{a} (72.63)	13.26 ^{a} (13.21)	0.02 and 0.05 (two s, 9H total, 1/1.7 ratio, Me$_3$Si), 0.67—1.47 (m, 13H, C$_6$H$_{13}$), 1.57—2.13 (m, 2H, SiCH$_2$), 5.08—5.47 (m, 2H, CH=CH) ^{a}
Me$_3$SiCH$_2$CH=C(CH$_2$)$_5$-cyclo	1.4678	72.74 (72.44)	12.21 (12.16)	0.03 (s, 9H, Me$_3$Si), 1.21—1.64 (broad m, 8H, with d at 1.42, ^3J(HH) 8.5Hz), (CH$_2$)$_3$ and SiCH$_2$), 1.87—2.21 (broad m, 4H, =C(CH$_2$)$_2$), 4.90—5.19 (broad t, ^3J(HH) 8.5 Hz, =CH)
	1.5248 ^{b}	known compound (cis/trans mixture) ^{b}		0.10 (s, 9H, Me$_3$Si), 1.59—1.71 (m with maxima at 1.59 and 1.71, 2H, SiCH$_2$), 6.10—6.27 (m, 2H, CH=CH), 7.20 (broad s, 5H, Ph) ^{c}
	1.5161			0.05 (s, 9H, Me$_3$Si), 1.82 (d of d, ^3J(HH) 9.0 Hz, ^4J(HH) 1.5 Hz, 2H, SiCH$_2$), 5.65 (d of t, 1/2 of AB pattern, J(AB) 12 Hz, ^3J(HH) 9 Hz, 1H, SiCH$_2$C*H*=), 6.35 (d of t, 1/2 of AB pattern, J(AB) 12 Hz, ^4J(HH) 1.5 Hz, 1H, PhC*H*=), 7.25 (broad s, 5H, Ph)
Me$_3$SiCH$_2$CH=C(CF$_3$)$_2$	1.3651	39.29 (38.39)	5.02 (4.83)	0.14 (s, 9H, Me$_3$Si), 2.00 (d of septets, ^3J(HH) 10.0 Hz, ^5J(FH) 2.0 Hz, 2H, SiCH$_2$), 6.77 (broad t, ^3J(HH) 10.0 Hz, 1H, CH=)
Me$_3$SiCH$_2$CH=C(C$_2$H$_5$)$_2$	1.4368	70.80 (70.49)	13.11 (13.02)	0.01 (s, 9H, Me$_3$Si), 0.91 (t, ^3J(HH) 7.0 Hz, 3H, CH$_3$ of Et), 0.93 (t, ^3J(HH) 7.0 Hz, 3H, CH$_3$ of Et), 1.36 (d, ^3J(HH) 8.5 Hz, 2H, SiCH$_2$), 1.94 (q, ^3J(HH) 7.0 Hz, 4H, CH$_2$ of Et), 5.04 broad t, ^3J(HH) 8.5 Hz, 1H, =CH)
	1.4365 ^{z} (n_D^{20})	known compound (unspecified isomer mixture) ^{c}		0.11 and 0.15 (two s, 54/46 ratio, 9H total, Me$_3$Si), 1.01 (broad t, 3H, CH$_3$ of Et), 1.51—1.77 (m, 5H, C=CCH$_3$ and SiCH$_2$), 1.91—2.11 (broad m, 2H, CH$_2$ of Et), 4.95 (broad t, 1H, CH=) ^{a}

(54/46 mixture of isomers)				
 [d]	1.5185	76.37 [a] (76.39)	9.99 [a] (9.86)	0.03 (s, 9H, Me_3Si), 1.83 (three peaks separated by ca. 1 Hz, 5H, $=C(CH_3)CH_2Si$), 6.11 (broad s, 1H, CH=), 7.13 (broad s, 5H, Ph)
 [d]	1.5220			0.13 (s, 9H, Me_3Si), 1.70 (d, $^4J(HH)$ 1Hz, 2H, $SiCH_2$), 1.87 (d, $^4J(HH)$ 1.6 Hz, 3H, CH_3), 6.08 (broad s, 1H, CH=), 7.14 (broad s, 5H, Ph)
$Me_2HSiCH_2CH{=}C(CH_2)_5$-cyclo [e]	1.4729	71.25 (71.34)	12.09 (11.98)	0.04 (d, $^3J(HH)$ 4 Hz, 6H, Me_2Si), 1.20–1.48 (m, 2H, $SiCH_2$), 1.50 (broad m, 6H, $(CH_2)_3$, 2.04 (broad m, 4H, $=C(CH_2)_2$, 3.81 (m, 1H, SiH), 5.03 (t, $^3J(HH)$ 8 Hz, =CH)
$Me_2HSiCH_2CH{=}C(C_2H_5)_2$	1.4390	69.20 (69.14)	13.00 (12.90)	–0.02 (d, $^3J(HH)$ 4 Hz, 6H, Me_2Si), 0.68 (t with fine splitting, $^3J(HH)$ 8 Hz, 6H, CH_3 of Et), 1.35 (d of d, $J(CH_2{-}SiH)$ 3 Hz, $J(CH_2{-}CH{=})$ 8 Hz, 2H, $SiCH_2$), 1.91 (q, $^3J(HH)$ 8 Hz, CH_2 of Et), 3.75 (m, 1H, SiH), 4.94 (t, $^3J(HH)$ 8 Hz, 1H, =CH)
$Me_3SiOSiMe_2CH_2CH{=}C(CH_2)_5$-cyclo	1.4490	60.96 (60.86)	11.04 (11.00)	0.05 (s, 6H, Me_2Si), 0.06 (s, 9H, Me_3Si), 1.40 (d, $^3J(HH)$ 8 Hz, 2H, $SiCH_2$), 1.52 (broad m, 6H, $(CH_2)_3$, 2.09 (broad m, 4H, $=C(CH_2)_2$, 5.04 (t, $^3J(HH)$ 8 Hz, 1H, =CH)

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[a] Obtained for the mixture of isomers. [b] Ref. 15 reports n_D^{25} 1.5252 for a mixture of the *cis* and *trans* isomers. [c] The IR spectrum (film) showed a strong band at 963 cm^{-1}, in confirmation of the *trans* configuration [14]. [d] Reported in ref. 16; n_D^{20} 1.4290 given. [e] ν(Si—H) 2120 cm^{-1}.

by the addition of 9.4 mmol of *n*-butyllithium in hexane to 10.6 mmol of diisopropylamine in 10 ml of diethyl ether at 0°C with subsequent at room temperature for 1 h. This solution of $i\text{-}Pr_2NLi$ was added dropwise, at 0°C under nitrogen, to a slurry of crude $[Ph_3PCH_2CH_2SiMe_2OSiMe_3]^+I^-$ (8.67 mmol) in 20 ml of diethyl ether. The mixture was stirred at room temperature for 1 h to give a homogeneous red solution of the ylide. Subsequently, 15.8 mmol of cyclohexanone was added dropwise. The reaction mixture was stirred at room temperature for 1 h and heated at reflux for 4 h. This treatment did not discharge the red color and therefore the mixture was stirred at room temperature for another 16 h. The resulting yellow mixture was filtered and the filtrate was trap-to-trap distilled in vacuo. GLC analysis of the distillate (SE-30 at 150°C) showed a 50% yield of $cyclo\text{-}(CH_2)_5C{=}CHCH_2SiMe_2OSiMe_3$.

$Ph_3P{=}C(C_6H_5)CH_2SiMe_3$

To an ice-cooled slurry of 6.04 g (10.7 mmol) of $[Ph_3PCH(C_6H_5)CH_2SiMe_3]^+I^-$ in 40 ml of THF was added dropwise with stirring, under nitrogen, 10.7 mmol of methyllithium in 7 ml of diethyl ether. The resulting red-brown yilide solution was stirred at room temperature for 1.5 h. It then was cooled to 0°C and 20 mmol of propionaldehyde was added. There was no observable reaction. As the reaction mixture was warmed to 40°C, it became colorless and a white, finely-divided precipitate formed. The latter was filtered and dried to give 5.95 g (98% recovery) of the starting phosphonium iodide, whose NMR spectrum and m.p. (182—184°) agreed with those of an authentic sample.

New compounds

The new compounds prepared in this study, together with their refractive indexes, analyses and proton NMR spectra, are listed in Table 2.

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