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Synthesis of Alkenes from Carbonyl Compounds and Carbanions α to Silicon. 6. Synthesis of Terminal Allenes and Allyl Chlorides[1,2]

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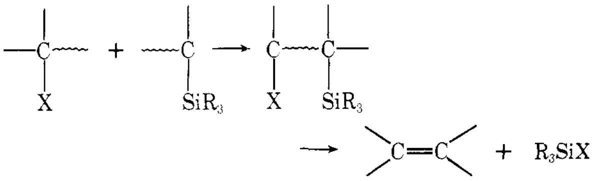
Aldehydes and ketones can be converted into terminal allenes or allylic chlorides by reactions with α-silylvinyl carbanions 2 followed by subsequent transformations. The mechanisms and the stereoselectivity of these reactions are discussed.

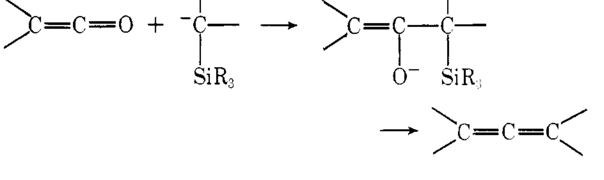
Reactions which lead to the synthesis of alkenes are of great importance to organic chemistry. Numerous named reactions (Hofmann, Saytzeff, Cope, Wittig) have been developed for this purpose. Recently, an alkene synthesis, based on the propensity of β-functionalized organosilicon compounds to undergo elimination, has been introduced.[3-5] The generality of the reaction can be expressed by eq 1 in that any



(1)

union of two fragments which brings together the β relationship of the silyl group and a good leaving group can be considered as an alkene synthesis.[5] A useful version of eq 1 involves the condensation of carbonyl compounds with carbanions α to silicon.[3-5] The reaction bears obvious similarity to the Wittig reaction[6] and its many modifications.

In the course of developing the synthetic utility of the silicon-based alkene synthesis, we became interested in extending the reaction to the preparation of allenes.[1] A priori, two approaches exist. One is to employ ketene as the starting material (eq 2), and the other is to react a carbonyl compound with a vinyl carbanion α to silicon (eq 3). We have chosen to explore the second approach (eq 3) not only because of the ready



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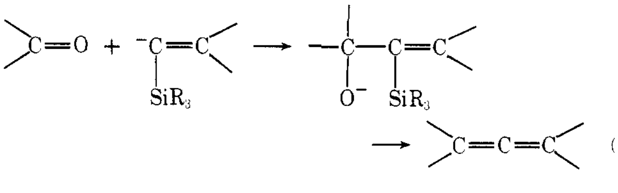

(3)

availability of the carbonyl compounds in general, but also because of the recognition that the vinylsilane moiety is a latent functionality which can be manipulated subsequently.[7]

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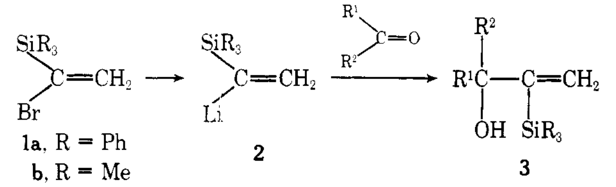
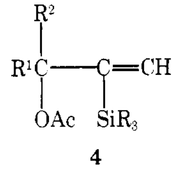
Results and Discussion

Synthesis of Terminal Allenes. Vinyl carbanions α to silicon could readily be generated from α-bromovinylsilanes either by a metal–halogen exchange reaction[8–10] or by reaction with magnesium.[9,11,12] We have used either α-bromovinyltriphenylsilane[8,9] (**1a**) or α-bromovinyltrimethylsilane (**1b**)[10,11] as the precursor. Reaction of **1a** with *n*-butyllithium at −24 °C, or **1b** with *tert*-butyllithium at −78 °C, gave the vinyl carbanions **2** in good yield. The vinyl carbanions reacted with a wide variety of carbonyl compounds to give the β-hydroxyvinylsilanes **3** in isolated yields ranging from 65 to 80%.[10,12] As expected, the trimethylsilyl compounds of **3** are more volatile and could be purified by distillation, whereas the triphenylsilyl compounds could be purified by crystallization if necessary. We found that it is easier to work with the trimethylsilyl series because the purity of each compound can be ascertained easily from the ^{1}H NMR spectrum by virtue of the sharp singlet due to the trimethylsilyl protons as well as by GC because of its volatility.


1a, R = Ph
b, R = Me
2
3

In view of the propensity of β-functionalized organosilicon compounds to undergo elimination, it was thought that these β-hydroxyvinylsilanes **3** should lead to allenes with little difficulty; surprisingly, this was not the case. For example, **3a** (R = R^1 = Ph; R^2 = H), when treated with dilute acid or sodium hydride, was recovered unchanged. The acetate derivative **4a** or the trifluoroacetate **5a** prepared from **3a** with the acid anhydride and pyridine were both resistant to elimination either on heating to 200 °C or dilute acid treatment. The trifluoroacetate **5a** did, however, hydrolyze quite readily, giving back the starting alcohol **3a**. The trifluoroacetates, in cases where they were derived from aliphatic ketones, underwent elimination of trifluoroacetic acid on warming to give a silyl diene (e.g., **5e** → **6e**). Treatment of the β-hydroxyvinylsilanes **3** with thionyl chloride afforded a mixture of chlorides **7–9** (eq 4). The relative proportions of each chloride depend on the structure of **3**, the solvent of reaction, as well as the temperature. Discussion on the rearrangement process will be deferred to the later part of the paper. It should be pointed out, however, that the conversion of **3** to **7** was found to be applicable only to **3** derived from aldehydes (i.e., R^2 = H) or aryl ketones (R^1 = R^2 = Ar). For β-hydroxyvinylsilanes **3** derived from aliphatic ketones, the products of thionyl chloride treatment were the dienes of structure **6**. The chlorides (**7–8**) did not give allene on heating to 175 °C or on treatment with alcoholic silver nitrate. The resistance to elimination must in part be due to the difficulty of cleaving the carbon–silicon bond in the vinyl system with nucleophiles. Indeed, nucleophilic cleavage of the silicon–vinyl carbon bond is rare in general.[13] Several reports have appeared in the literature to indicate that fluoride ion may be a particularly effective nucleophile for such cleavage. It has been known that fluoride ion can cleave the silicon–alkynyl carbon bond.[14] More pertinent was the report by Cunico and Dexheimer[15] which showed that fluoride can effect the β elimination of β-chlorovinyltrimethylsilane to give acetylene (eq 5).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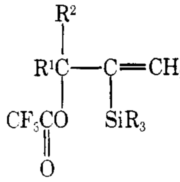
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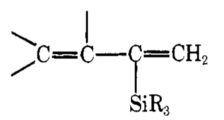
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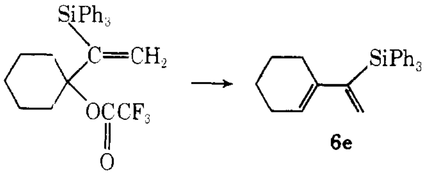
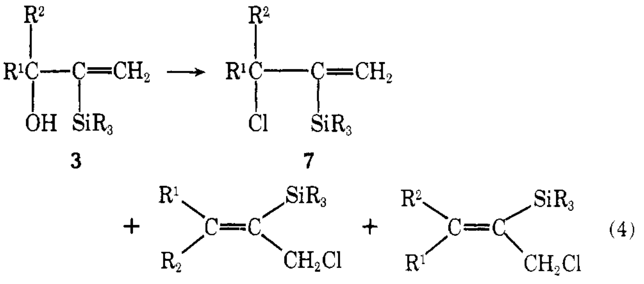

5e
6e

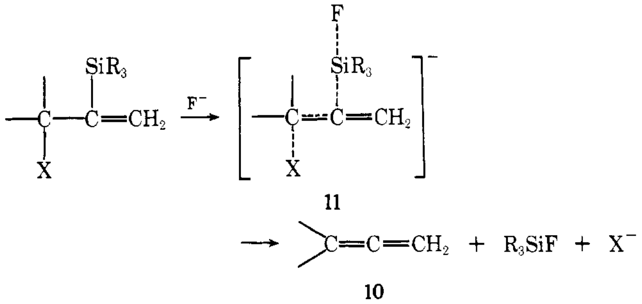

3
7
8
9
(4)

$$\mathrm{CHCl = CHSiMe_3 + F^- \rightarrow HC{\equiv}CH + Me_3SiF + Cl^-} \quad (5)$$

We thus attempted the β elimination of the vinylsilyl system (**7–9**) with fluoride ion and the results were most satisfying. When compound **7a** was dissolved in either Me$_2$SO or CH$_3$CN with some anhydrous fluoride salt at room temperature, it was transformed quantitatively to phenylallene (**10a**). The order of efficacy of the fluoride salts appears to be tetraalkylammonium fluoride (R$_4$NF, R = CH$_3$ or C$_2$H$_5$ or *n*-C$_4$H$_9$) > cesium fluoride > potassium fluoride. This may simply be a reflection of the order of solubilities of the salts in organic solvent. Other halides are not effective in promoting the elimination. Treatment of **7a** with tetraethylammonium chloride, bromide, or iodide under identical or more forcing conditions gave no allene and the starting materials were recovered quantiatively.

The nature of the substituents on the silyl group have some effect on the rate of elimination. Under identical conditions, the triphenylsilyl compound **7a** underwent elimination five times faster than the corresponding trimethylsilyl compound **7g**. The rate of formation of allene is also dependent upon the nature of the leaving group. The trifluoroacetate **5a** eliminated to give phenylallene cleanly, albeit slightly slower than the chloride **7a**. The acetate **4a**, on the other hand, did not eliminate at room temperature in Me$_2$SO in the presence of fluoride ion. Only on heating to 150 °C did elimination occur to give phenylallene.

A possible mechanism which is compatible with all these observations can involve a rate-determining step where formation of the silicon–fluoride bond is concerted with the breakage of the silicon–carbon bond as well as the departure of the leaving group (**11**).[16,17] The difference in reactivity between the triphenylsilyl and the trimethylsilyl groups can


11
10

be explained by the argument that methyl is electron donating and the trimethylsilyl group is thus less susceptible to attack by the fluoride ion.

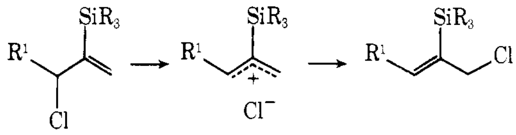
A number of allenes have been prepared by this method from the starting carbonyl compounds (Table III). The convenience of the procedure is enhanced by carrying out the preparation without purification of the intermediate chlorides **7**–**9**. In cases where the chlorides could not be prepared, the trifluoroacetates **5** could be used as the precursors to allenes. The yields of the allenes obtained were nearly the same whether the triphenylsilyl compounds or the trimethylsilyl compounds were used. It was, however, easier to use the trimethylsilyl compounds because in the final purification of allenes the other product of the reaction, trimethylfluorosilane, was volatile and could be removed with ease.

We have so far applied this method to the preparation of 1,2-alkadienes. With the availability of α-silylalkenyl carbanions,[18,19] there is no apparent reason why the reaction could not be applied to nonterminal allenes.

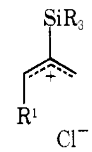
The advantages of the present method appear to be: (1) the starting carbonyl compounds are in general readily available; (2) a double bond elsewhere in the molecule is not affected (e.g., **9d** and **9f**); and (3) more importantly, because of the mild conditions in the allene generation step, the allenes produced were free of contamination by the isomeric acetylenes. Most other methods for synthesizing allenes result in acetylenic impurities in the product due to isomerization of the allenes under strongly basic conditions often employed.[20,21] No such problem exists by utilizing the silicon method, since strong base is not employed in the final step.

Conversion of R^1CHO into $R^1CH{=}CHCH_2Cl$. The reactions of the β-hydroxyvinylsilanes **3** with thionyl chloride to give a mixture of allylic chlorides **7**–**9** (eq 4) deserve closer scrutiny. The formation of the three isomeric chlorides was of course not unexpected in view of the familiar allylic rearrangement.[22,23] What is interesting is the subtle variation of the relative proportions of the chlorides **7**–**9** with solvent and structural parameters in this reaction. We have investigated in some detail the chlorination reactions of **3** derived from aldehydes and trimethylvinyl carbanion (i.e., **3**, R^2 = H; R = CH_3). In general, the rearranged chlorides (**8** and **9**), being more substituted, are more stable than the nonrearranged chloride (**7**), which has a terminal double bond. The rearranged chlorides (**8** and **9**) were indeed formed to the greater extent, often to the exclusion of **7**, if the chlorination were carried out in a polar solvent (e.g., ether) or if the products were allowed to be equilibrated thermally (by heating to 140 °C for 2–3 h). In specific cases, however, with the use of a nonpolar solvent (e.g., CCl_4) at room temperature it was possible to obtain pure **7**. For example, treatment of the compound **3a** with thionyl chloride in carbon tetrachloride gave chloride **7a** in quantitative yield. However, when this chloride was dissolved in dimethyl sulfoxide or heated, an allylic rearrangement occurred giving **8a** exclusively.

These observations are consistent with an ionic mechanism for the allylic rearrangement. In a medium of higher solvating power, formation of what was probably an intimate ion pair **12a** took place. Internal return of the chloride ion would give **8** regioselectively. In addition to being regioselective, the rearrangement is often highly stereoselective, giving predominantly the *Z* isomer **8** with the *E* isomer **9** present in most cases in <10%. The stereoselectivity may be due to the preference of the intermediate carbenium ion for the transoid configuration (**12a**)[24] rather than the cisoid configuration (**12b**).

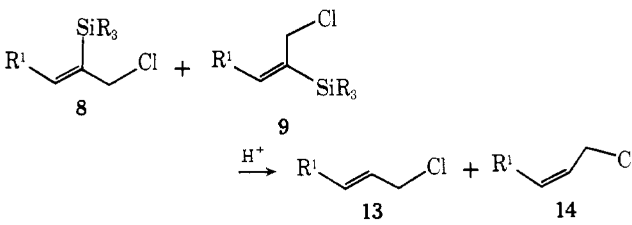


12a

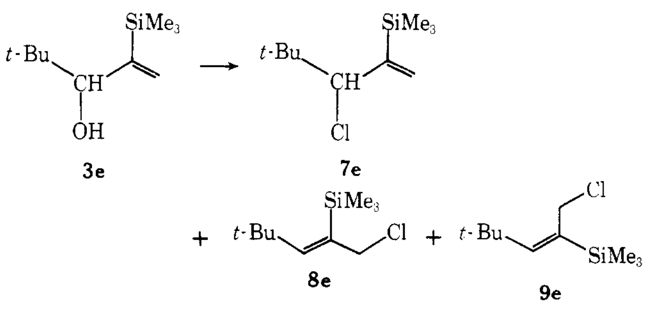


12b

The assignment of *Z* stereochemistry to the major isomer in the mixture **8** and **9** rests on ^1H NMR evidence[25] as well as on chemical transformation. The replacement of the trimethylsilyl group in vinylsilanes by a proton under electrophilic conditions has been firmly established to proceed with retention of stereochemistry.[26,27] Thus, the mixture chlorides **8** and **9**, on reaction with gaseous HCl in chloroform, was converted in good yield to the olefins **13** and **14**. The major isomer **13** was assigned to be *E* on the basis of the coupling constant (15–19 Hz) of the olefinic protons in the 220-MHz spectrum. The assignment was also supported by their infrared spectra where the prominent band at ~960 cm^{-1} was observed. The presence of the minor *Z* isomer (**14**) was also evident from the 220-MHz ^1H NMR spectra and the relative ratio of the *E*/*Z* isomers could be deduced (Table IV). The protodesilylation reactions not only establish the stereochemistry of the chloride, but also constitute a viable method of transforming stereoselective R^1CHO into (*E*)-$R^1CH{=}CHCH_2Cl$ (**3** → **8** → **13**).[1b]

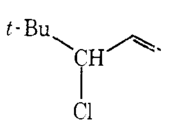


The stereoselectivity of the conversion of R^1CHO to $R^1CH{=}CHCH_2Cl$ depends obviously on the relative proportion of **8** and **9** during the thionyl chloride reaction. It would seem that the structure of R should play a role in determining the extent of stereoselectivity. For R being aryl and most aliphatic groups, the isomer **8** predominates. However, if R^1 is sufficiently bulky, one would expect steric interaction between R^1 and the trimethylsilyl group to be sufficient to render **8** to be the less favored isomer. Such is the case when R^1 is the *tert*-butyl group. When β-hydroxyvinylsilane **3l** was treated with thionyl chloride in ether, chlorination did occur; however, the three isomers **7l**, **8l**, and **9l** were obtained in a ratio of 1:4:3, respectively, according to ^1H NMR and VPC analysis. Furthermore, when the reaction mixture was heated neat to 150 °C for a period of 3 h the ratio of isomers changed to **7l**/**8l**/**9l** = 3:0:2. No further change of isomeric ratio was observed on prolonged heating. It is clear that the steric interaction of the trimethylsilyl group with the *tert*-butyl group modifies somewhat the relative stabilities of the isomers.

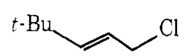


Treatment of the original mixture of isomers (i.e., **7l**/**8l**/**9l** = 1:4:3) with HI afforded a mixture of olefins **15h**, **13h**, and **14h** in a ratio identical with that of the starting vinylsilanes. Treatment of this same isomeric mixture of vinylsilanes with trifluoroacetic acid gave, however, only **13h** and **14h** with little **15h**. The terminal vinylsilane **7l** is apparently more resistant to electrophilic substitution than the nonterminal ones. On further standing in TFA, compound **7l** did disappear, but not to the corresponding olefin **15h**. Instead, it appeared to rearrange slowly to **8l**–**9l** and then underwent protodesilylation to give **13h** and **14h** only.

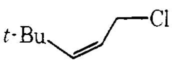
An interesting possibility thus presented itself by these results. It would seem that it is possible to produce the *Z* isomer **14h** stereoselectively under these conditions even though it is thermodynamically less stable. Indeed, on treating the heated vinylsilane mixture (i.e., **7l**/**8l**/**9l** = 3:0:2) with TFA, the olefin obtained was predominantly **14h** (85% Z). The overall result is therefore the stereoselective conversion of pivaldehyde into the sterically less favored *Z* olefin **14h**.[28]



15h



13h



14h

Summary

Methods have been found which permit the conversion of carbonyl compounds into terminal allenes. The stereoselective transformations of aldehydes into RCH=CHCH$_2$Cl has also been described. The relative stability of β-functionalized vinylsilanes (**3**, **4**, **7**, **8**, and **9**) to elimination, together with the observation that fluoride ion can promote such elimination easily, have some interesting consequences. For example, it is possible to modify the vinylsilyl group of **7** into an epoxysilyl group by epoxidation of the double bond, and subsequently promote the β elimination of halosilane by fluoride ion, thus generating reactive allene oxides.[29] Another feature of the present work is the recognition that the silyl group can serve as a device for stereochemical control in the synthesis of alkenes (e.g., RCH=CHCH$_2$Cl). The silyl group can subsequently be displaced by proton or other electrophiles, thus paving the way for the stereoselective synthesis of di-, tri-, and tetrasubstituted alkenes.[30]

Experimental Section

Common chemicals were obtained from commercial sources and were purified as necessary. Melting points were obtained on a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer Model 257 or Unicam SP1000 grating infrared spectrometers. Spectra were calibrated with the 1601-cm^{-1} band of polystyrene film. Nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Varian Associates T-60 or HR-220 spectrometers as indicated. Mass spectra were recorded either by direct insertion on an E A1-MS-902 mass spectrometer or by GC–MS with an LKB-9000 spectrometer at 70 eV. Microanalyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark. Gas chromatographic (GC) analyses were performed on an F&M Model 5751-A research chromatograph. Two 6 ft × 1/8 in. stainless steel columns were used: 10% SE-30 Ultraphase on Chromosorb W A/W-DMCS, or 10% Apiezon-L on Chromosorb W A/W-DMCS. Preparative thin-layer and column chromatography were done on silica gel.

α-Bromovinyltriphenylsilane (1a). The title compound was prepared according to the literature procedure.[8] It had mp 132–134 °C (lit.[8] mp 128–129 °C).

α-Bromovinyltrimethylsilane (1b). To a solution of 0.5 mol of trichlorovinylsilane in 500 mL of CCl$_4$ irradiated with a daylight lamp was added dropwise a solution of 0.5 mol of Br$_2$ in 100 mL of CCl$_4$ over a period of 1–2 h. Occasional cooling was necessary as the reaction was highly exothermic. After the addition, the mixture was stirred for 1 h, and the solvent was then removed. To the solvent-free mixture was added slowly 0.65 mol of quinoline, and the reaction mixture was distilled at reduced pressure to give α-bromovinyltrichlorosilane in 82% yield [bp 70–71 °C (53 mm); lit.[29] bp 145.4 °C (749 mm)].

To a solution of CH$_3$MgI in 1.5 L of anhydrous ether (prepared from 1.5 mol of CH$_3$I and 37 g of Mg in 1.5 L of anhydrous ether) was added dropwise a solution of 0.4 mol of α-bromotrichlorovinylsilane in 500 mL of anhydrous ether over a period of 2 h. After the addition, the reaction mixture was heated under reflux for another 5 h. The reaction mixture was hydrolyzed with water, and then dried with anhydrous MgSO$_4$. Removal of the solvent from the reaction mixture, followed by fractional distillation at reduced pressure, gave the desired α-bromovinyltrimethylsilane in 70% yield [bp 56.7 °C (67 mm); lit.[11] bp 26–27 °C (15 mm)].

1-Substituted-2-trisubstituted-silyl-2-propen-1-ols (3). The title alcohols were prepared from the reaction of α-silylvinyl carbanions[8] with appropriate carbonyl compounds. The following is a general procedure for the preparation of the triphenylsilyl compounds (**3a–f**).

To a solution of 0.025 mol of α-bromovinyltriphenylsilane in 60 mL of anhydrous ether at −24 °C (dry ice–CCl$_4$ bath) under a N$_2$ atmosphere was added slowly, by means of a syringe, a solution of 0.025 mol of *n*-butyllithium. The resulting mixture was kept stirred at the same temperature for 1.5 h. A solution of 0.025 mol of carbonyl compound in 10 mL of dried ether was added. The reaction mixture was stirred at −24 °C for 5 h, then stirring was continued overnight at room temperature. The reaction mixture was poured into 50 mL of 10% HCl and the organic phase was extracted, dried, and evaporated to give the desired alcohol (Table I).

Following is a general procedure for the preparation of the trimethylsilyl compounds (**3g–l**).

To a solution of 0.05 mol of α-bromovinyltrimethylsilane in 150 mL of anhydrous ether at −78 °C under a N$_2$ atmosphere was added slowly by means of a syringe a solution of 0.052 mol of *tert*-butyllithium in pentane.[10] The resulting mixture was kept well stirred at the same temperature for 2 h. A solution of 0.05 mol of carbonyl compound in 10 mL of anhydrous ether was added. The reaction mixture was stirred at −78 °C for another hour and was then allowed to warm up to room temperature by itself. After hydrolysis (50 mL of water) and drying with anhydrous MgSO$_4$, the reaction mixture was reduced in volume in vacuo and fractionally distilled at low pressure to give the desired alcohol (Table I).

Reaction of 1-Substituted-2-silyl-2-propen-1-ols (3) with Acetic Anhydride/Pyridine. To a solution of 50 mmol of the alcohol **3** in 10 mL of pyridine at room temperature was added dropwise 5.0 g of acetic anhydride (10% excess). The reaction was exothermic. The mixture was heated under reflux for 2 h, cooled, and poured into 20 mL of water. The reaction mixture was extracted with 2 × 20 mL of ether. The ether solution was dried over anhydrous MgSO$_4$ and evaporated in vacuo to give the corresponding acetates **4** in quantitative yields.

The following acetates have been prepared. They all have proper spectroscopic and/or analytical data consistent with structures: 3-acetoxy-3-phenyl-2-triphenylsilyl-1-propene (**4a**), mp 90–91 °C (hexane); 3-acetoxy-3-cyclohexyl-2-trimethylsilyl-1-propene (**4j**), bp 76–78 °C (0.1 mm); 3-acetoxy-4-methyl-2-trimethylsilyl-1-pentene (**4k**), bp 54–56 °C (0.75 mm); 3-acetoxy-2-trimethylsilyl-1-tridecene (**4c**), bp 104–106 °C (0.1 mm); 3-acetoxy-3,3-diphenyl-2-triphenylsilyl-1-propene (**4b**), mp 164–167 °C (EtOH).

Reaction of 1-Substituted-2-silyl-2-propen-1-ols (3) with Trifluoroacetic Anhydride/Pyridine. To a solution of 50 mmol of the alcohol **3** in 10 mL of pyridine at 0 °C was added dropwise 12 g of trifluoroacetic anhydride (10% excess). The reaction mixture was stirred at room temperature for 2 h, poured into 20 mL of water, and extracted with 2 × 20 mL of ether. The organic solution was dried over anhydrous MgSO$_4$ and evaporated in vacuo to give the corresponding acetates **5** in quantitative yield. No further purification of these compounds was undertaken.

1-Trifluoroacetoxy-1-phenyl-2-triphenylsilyl-2-propene (5a): IR (CCl$_4$) 1780 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 5.95 (m, 1 H), 6.35 (m, 1 H), 6.55 (m, 1 H), 7.2–7.8 (m, 20 H).

1-(α-Trifluoroacetoxycyclohexyl)-1-triphenylsilylethylene (5e): IR (CCl$_4$) 1785 cm^{-1}; ^{1}H NMR (CCl$_4$) 0.9–2.5 (m, 11 H), 5.85 (AB, 2 H), 7.2–7.8 (m, 15 H). When this trifluoroacetate was dissolved in Me$_2$SO, heated on a steam bath to aid dissolving, a precipitate formed. The mixture was poured into water and extracted with ether. The ether solution was dried over MgSO$_4$ and evaporated in vacuo. Recrystallization of the residue from EtOH gave a solid, mp 89–93 °C, assigned to be **1-cyclohexenyl-1-triphenylsilylethylene (6e):** IR (KBr) 2920, 1435, 1115, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1–2.5 (m, 6 H), 5.4 (d, *J* = 2.5 Hz, 1 H), 5.76 (m, 1 H), 6.08 (d, *J* = 2.5 Hz, 1 H), 7.2–7.8 (m, 15 H).

Table I. Physical Data and Yields of 3

	R	R[1]	R[2]	Registry no.	Mp or bp, °C (mmHg)	Yield, %	^1H NMR, δ	Analyses
3a	Ph	Ph	H	52629-60-4	84–85	75	1.8 (s, 1 H), 5.5 (t, 1 H), 5.8 (t, 1 H), 6.2 (t, 1 H), 7.2–7.8 (m, 20 H)	C,H
3b	Ph	Ph	Ph	52629-61-5	108.5–109.5	80	2.6 (s, 1 H), 5.7 (d, 1 H), 5.9 (d, 1 H), 7.2–7.8 (m, 25 H)	C,H
3c	Ph	n-$C_{10}H_{21}$	H	52629-62-6	*a*	75	0.9–1.6 (m, 22 H), 4.2 (m, 1 H), 5.5 (m, 1 H), 6.2 (m, 1 H), 7.2–7.5 (m, 15 H)	*b*
3d	Ph	$C_6H_5CH{=}CH$-	H	65071-60-5	*a*	80	5.0 (m, 1 H), 5.7–6.5 (m, 4 H), 7.2–7.8 (m, 20 H)	*b*
3e	Ph	c-C_5H_{10}		65071-61-6	*a*	75	0.9–2.4 (m, 11 H), 5.5 (d, 1 H), 6.00 (d, 1 H), 7.2–7.8 (m, 15 H)	*c*
3f	Ph	CH_3	$(CH_3)_2C{=}CH(CH_2)_2$–	65071-62-7	*a*	75	0.9–2.5 (m, 14 H), 5.0 (b, 1 H), 5.6 (d, 1 H), 7.2–7.8 (m, 15 H)	*c*
3g	Me	Ph	H	5166-96-7	82–84 (0.9)	80	0.15 (s, 9 H), 3.7 (s, 1 H), 5.5 (m, 1 H), 6.0 (AB, 2 H), 7.6 (s, 5 H)	*c*
3h	Me	Ph	Ph	51666-98-9	*a*	80	0.2 (s, 9 H), 3.0 (s, 1 H), 5.5 (AB, 2 H), 7.4 (s, 1 H)	*c*
3i	Me	n-$C_{10}H_{21}$	H	58672-92-7	118–119 (0.03)	75	0.1 (s, 9 H), 0.7–1.7 (m, 21 H), 1.9 (s, 1 H), 4.15 (t, 1 H), 5.5 (AB, 2 H)	C,H
3j	Me	c-C_6H_{11}	H	58649-14-2	64–66 (0.025)	75	0.2 (s, 9 H), 0.8–2.15 (m, 12 H), 3.85 d, 1 H), 5.45 (AB, 2 H)	*c*
3k	Me	i-Pr	H	58649-15-3	82–84 (16)	76	0.1 (s, 9 H), 0.9 (d, 6 H), 1.5–2.0 (m, 2 H), 3.85 (d, 1 H), 5.55 (AB, 2 H)	*c*
3l	Me	t-Bu	H	61628-61-3	69–71 (5)	79	0.15 (s, 9 H), 0.9 (s, 9 H), 1.85 (b, 1 H) 3.90 (s, 1 H), 5.6 (AB, 2 H)	C,H

[a] Purified by column chromatography. Purity ascertained by TLC or GC. [b] Exact mass of the molecular ion to within ±10 ppm. [c] Molecular weight established by low-resolution mass spectrum.

Table II. Physical Data of Isomeric Chlorides 7–9

Registry no.	R	R[1]	R[2]		Mp or bp, °C (mmHg)	^1H NMR, δ	Analyses
52629-67-1	Ph	Ph	H	**7a**	148–149	5.85 (AB, 2 H), 6.7 (t, 1 H), 7.5 (s, 5 H), 7.1–7.8 (m, 15 H)	C,H
65071-63-8	Ph	Ph	H	**8a**	148–149	4.25 (s, 2 H), 6.6 (s, 1 H), 7.0–7.8 (m, 20 H)	C,H
52629-69-3	Ph	Ph	Ph	**8b**	147–148	4.2 (s, 2 H), 6.6–7.8 (m, 25 H)	*b*
65085-85-0	Ph	n-$C_{10}H_{21}$	H	**8c**	*a*	0.9–2.1 (m, 21 H), 4.15 (s, 2 H), 6.85 (t, 1 H), 7.2–7.8 (m, 15 H)	*b*
65071-64-9	Ph	$PhCH{=}CH$–	H	**8d**	*a*	4.19 (s, 2 H), 6.4–7.8 (m, 23 H)	*b*
55287-91-7	Me	Ph	H	**7g**	*c*	0.1 (s, 9 H), 5.65 (m, 2 H), 6.1 (m, 1 H), 7.2 (s, 5 H)	*b*
58844-31-8				**8g**	89–90 (1.5)	0.2 (s, 9 H), 4.2 (s, 2 H), 6.8 (s, 1 H), 7.0–7.4 (m, 5 H)	C,H
58649-16-4	Me	n-$C_{10}H_{21}$	H	**8i**	90–100 (0.05)	0.22 (s, 9 H), 0.7–2.3 (m, 21 H), 3.9 (s, 2 H), 6.28 (t, 1 H)	C,H
58649-17-5	Me	c-C_6H_{11}	H	**8j** + **9j** (~90:10)	66–67 (0.35)	**8j**: 0.22 (s, 9 H), 0.7–2.3 (m, 11 H), 4.0 (s, 2 H), 6.08 (d, 1 H)	C,H
64645-72-3						**9j**: 0.14 (s), 0.7–2.3 (m), 4.05 (s), 5.78 (d)	
58649-18-6	Me	i-Pr	H	**8k** + **9k** (~85:15)	73–75 (12)	**8k**: 0.22 (s, 9 H), 1.05 (d, 6 H), 2.6 (m, 1 H), 4.05 (s, 2 H), 6.08 (d, 1 H)	C,H
64645-71-2						**9k**: 0.14 (s), 1.05 (d), 2.6 (m), 4.1 (s), 5.78 (d)	
61628-64-6	Me	t-Bu	H	**7l** + **8l** + **9l**[d]	90–97 (14)	**7l**: 0.16 (s, 9 H), 1.0 (s, 9 H), 4.25 (b, 1 H), 5.5 (d, 1 H), 5.8 (bd, 1 H)	
61628-62-4						**8l**: 0.30 (s, 9 H), 1.15 (s, 9 H), 4.05 (s, 2 H), 6.35 (s, 1 H)	C,H
61628-63-5						**9l**: 0.15 (s, 9 H), 1.2 (s, 9 H), 4.2 (s, 2 H), 5.75 (s, 1 H)	

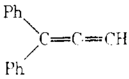
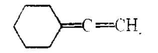
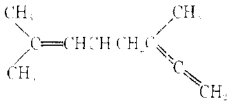
[a] Not crystalline. [b] Molecular weight determined by low-resolution mass spectrum. [c] Rearranged to **8g** on distillation. [d] Proportions varied; see text.

3-Trifluoroacetoxy-3,7-dimethyl-2-triphenylsilyl-1,6-octadiene (5f): IR (CCl_4) 1760 cm^{-1}; ^1H NMR (CCl_4) δ 1.2–2.3 (m, 13 H), 4.8 (m, 1 H), 5.9 (AB, 2 H), 7.2–7.8 (m, 15).

Reaction of 1-Substituted-2-silyl-2-propen-1-ols (3) with Thionyl Chloride. To a solution of 50 mmol of alcohol **3** in 40 mL of CCl_4 (or Et_2O) at room temperature was added dropwise a solution of 7.1 g of $SOCl_2$ (20% excess) in 20 mL of CCl_4 (or Et_2O). The reaction was exothermic and an ice bath was used occasionally to cool down the reaction mixture to below room temperature. The reaction mixture was generally kept well stirred for 2 h before workup. The solvent was evaporated under vacuo to give a residue which was purified by either recrystallization or distillation (Table II).

Fluoride Ion Promoted Formation of Terminal Allenes. General Procedure. To a solution of 0.02 mol of β-functionalized silane (**5**, **7**, **8**, or **9**) in 15–20 mL of solvent (Me_2SO or CH_3CN) was added 0.025 mol of inorganic fluoride (tetraalkylammonium, potassium or cesium fluoride). The reaction mixture was stirred for 2–10 h, poured into 20 mL of water, washed with 2 × 10 mL of water, dried

Table III. Preparation of 1,2-Alkadienes (9)

	1,2-Alkadiene	Registry no.	Method[a]	Isolated yield,[b] %	Bp, °C (mmHg)	IR, cm^{-1}	^{1}H NMR, δ
9a	$PhCH{=}C{=}CH_2$	2327-99-3	A B	59 60	83–85 (2.4)	*c*	*c*
9b		14251-57-1	A B	45[d] 30	100 (0.025)	*e*	*e*
9c	$n\text{-}C_{10}H_{21}CH{=}C{=}CH_2$	52629-63-7	A B	44 48	63–64 (0.1)	1960	0.75–2.25 (m, 21 H), 4.6 (m, 2 H), 5.05 (m, 1 H)
9d	$PhCH{=}CH\text{-}CH{=}C{=}CH_2$	65071-53-6	A	35	70–75 (0.075)	1960	4.9 (d, 2 H), 5.65–6.8 (ABC, 3 H), 7.1–7.6 (m, 5 H)
9e		5664-20-0	C	20	*f*	1955	1.1–2.3 (m, 10 H), 4.4 (m, 2 H)
9f		65071-54-7	C	20	*f*	1955	1.5 (s, 3 H), 1.6 (s, 3 H), 1.5–2.3 (m, 7 H), 4.4 (m, 2 H), 4.95 (m, 1 H)

[a] Method A, triphenylsilyl adduct and via chlorination; method B, trimethylsilyl adduct and via chlorination; method C, triphenylsilyl adduct and via trifluoroacetylation. [b] Isolated yield based on starting carbonyl compound. [c] Compared with authentic sample synthesized according to J. Hayami, N. Oko, and A. Kaji, *Tetrahedron Lett.*, 1385 (1968). [d] Purified by thin layer chromatography. [e] Compared with authentic sample prepared according to ref 21. [f] Purified by bulb-to-bulb distillation.

Table IV. Preparation of 13 and 14 by the Protodesilylation of Vinylsilanes 8 and 9

R^1	Bp, °C (mmHg)	Yield[a]	*J* of olefinic protons of major isomer, Hz[b]	*E/Z*[b]	Analysis
C_6H_5	*c*	90[d]	*c*	*c*	*c*
$n\text{-}C_{10}H_{21}$	76–77 (0.06)	74 (66)	15	85/15	*e*
$c\text{-}C_6H_{11}$	53 (1.3)	65 (62)	18.8	85/15	*e*
i-Pr	58–60 (89)	75 (45)[f]	15.3	90/10	*e*

[a] Yield determined by VPC with isolated yield in parentheses. [b] Determined from 220 MHz proton NMR spectrum. [c] Compound compared with authentic sample. [d] ^{1}H NMR showed that cinnamyl chloride was the sole compound in the product. [e] Analyzed by exact mass to within ±10 ppm of calculated mass of the molecular ion. [f] Lower isolated yield due to loss in distillation because of the low boiling point of the compound.

over anhydrous $MgSO_4$, and evaporated in vacuo. The product was subsequently purified by distillation under reduced pressure.

Synthesis of 1,2-Alkadienes from Carbonyl Compounds without Purification of Intermediate Steps. The carbonyl compounds were reacted with α-silylvinyl carbanions to give the alcohols 3 as previously described. The alcohols were used without purification for $SOCl_2$ reaction or trifluoroacetylation using procedures as described. Again, the products were not purified. Elimination with fluoride ion was carried out (vide supra). A typical procedure is outlined below.

Synthesis of 1,2-Tridecadiene. To a solution of 8.8 g (0.024 mol) of α-bromovinyltriphenylsilane in 60 mL of anhydrous ether at −24 °C, an equimolar amount of *n*-butyllithium was added slowly and stirred for 1–1.5 h. An equimolar amount of undecanal in 10 mL of ether was added slowly and the reaction mixture was stirred at −24 °C for 1 h. The stirring was continued at room temperature overnight. The reaction mixture was poured into 50 mL of 10% HCl and the organic phase was extracted and washed with 1 × 50 mL of water, dried over anhydrous $MgSO_4$, and evaporated in vacuo to give the crude product **3c**. The crude alcohol was dissolved in 25 mL of CCl_4 and a 25% excess of thionyl chloride was added. The reaction was stirred for 2 h and then evaporated in vacuo to give the crude chloride **8c**. The crude chloride was dissolved in Me_2SO (25 mL/g of Et_4NF) and Et_4NF was added (10% excess). The mixture was sitrred for 2 h at room temperature. The reaction mixture was portioned between 25 mL of ether and 25 mL of water. The ether phase was dried over $MgSO_4$ and evaporated in vacuo to give crude product. The crude product was treated with 10 mL of hexane and cooled. Filtration gave triphenylsilanol; distillation of the filtrate gave 1,2-tridecadiene, bp 63–64 °C (0.1 mmHg), in 44% yield. Similar procedures were followed for the other allenes (Table III). For the trimethylsilyl adducts the hexane precipitation step was omitted.

Reaction of 1-Substituted-3-chloro-2-trimethylsilyl-1-propene (8 and 9) with Gaseous Hydrogen Chloride. Dried gaseous HCl was bubbled into a solution of **8** and **9** (1 g) in 10 mL of chloroform for ~5 min. The mixture was stirred at room temperature for 2–5 days. The reaction mixture was followed by GC analysis, which revealed the formation of the desilylated products **13** and **14**. The products were purified by distillation at reduced pressure (Table IV).

Reaction of 1-Chloro-4,4-dimethyl-2-trimethylsilyl-2-pentenes (8h and 9h) and 3-Chloro-4,4-dimethyl-2-trimethylsilyl-1-pentene (7h) with Trifluoroacetic Acid. To a solution of 0.2 g of a mixture of **7h**, **8h**, and **9h** in 5 mL of $CHCl_3$ was added 0.2 g of trifluoroacetic acid and the solution was stirred at room temperature for 2 days. The reaction mixture was poured into 10 mL of water, washed with 10 mL of 10% $NaHCO_3$, dried over anhydrous $MgSO_4$, and evaporated under vacuo to give the allylic chlorides **13h** and **14h**. The allylic chlorides **13h** and **14h** had spectroscopic properties identical with those reported in the literature.[28]

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Registry No.—**1a,** 18676-45-4; **1b,** 13683-41-5; **4a,** 52629-65-9; **4b,** 65071-55-8; **4c,** 65071-56-9; **4j,** 62527-81-5; **4k,** 62527-82-6; **5a,** 52629-66-0; **5e,** 65071-57-0; **5f,** 65071-58-1; **6e,** 65085-86-1; 13 (R^1 = $C_{10}H_{21}$), 58649-19-7; 13 (R^1 = c-C_6H_{11}), 58649-21-1; 13 (R^1 = *i*-Pr), 58649-23-3; 14 (R^1 = $C_{10}H_{21}$), 58649-20-0; 14 (R^1 = c-C_6H_{11}), 58649-22-2; 14 (R^1 = *i*-Pr), 58649-24-4; $R^1R^2C{=}O$ (R^1 = Ph; R^2 = H), 100-52-7; $R^1R^2C{=}O$ (R^1,R^2 = Ph), 119-61-9; $R^1R^2C{=}O$ (R^1 = $C_{10}H_{21}$;

R_2 = H), 112-44-7; $R^1R^2C{=}O$ (R^1 = PhCH=CH; R_2 = H), 14371-10-9; $R^1R^2C{=}O$ (R^1,R^2 = c-C_5H_{10}), 108-94-1; $R^1R^2C{=}O$ (R^1 = CH_3; R^2 = $Me_2C{=}CH(CH_2)_2$), 110-93-0; $R^1R^2C{=}O$ (R^1 = c-C_6H_{11}; R^2 = H), 2043-61-0; $R^1R^2C{=}O$ (R^1 = *i*-Pr; R^2 = H), 78-84-2; $R^1R^2C{=}O$ (R^1 = *t*-Bu; R^2 = H), 630-19-3; trichlorovinylsilane, 75-94-5; α-bromovinyltrichlorosilane, 18038-34-1; acetic anhydride, 108-24-7; trifluoroacetic anhydride, 407-25-0; $SOCl_2$, 7719-09-7.

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Oxidation of Hydrocarbons. 8. Use of Dimethyl Polyethylene Glycol as a Phase Transfer Agent for the Oxidation of Alkenes by Potassium Permanganate[1a]

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Dimethyl polyethylene glycol solubilizes potassium permanganate in benzene or methylene chloride and can thus be used as a phase transfer agent for permanganate oxidations. If benzene is used as the solvent, dimethyl polyethylene glycol will not efficiently extract potassium permanganate from an aqueous solution, but it will solubilize the solid reagent. When methylene chloride is used as the solvent, potassium permanganate may be transferred from either an aqueous solution or from the solid phase. The products obtained from the oxidation of terminal alkenes were found to be the corresponding carboxylic acids with one less carbon, while nonterminal alkenes gave diones, diols, and ketols as well as carboxylic acids. The distribution of products may be controlled through selection of the appropriate conditions. A comparison has been made with the use of a quaternary ammonium ion, a crown ether, and acyclic polyethers as phase transfer agents for the oxidation of alkenes by permanganate.

Historically the use of permanganate ion as an oxidant for hydrocarbons has been limited because of its low solubility in most nonpolar solvents.[1b] However, the observation that potassium permanganate could be extracted from water into benzene by use of phase transfer agents substantially increased the potential usefulness of this reagent. The first phase transfer agent used was tricaprylmethylammonium chloride.[2] Since that time other ammonium[3–5] and arsonium[6] salts have been used with varying degrees of success. In 1967 Pedersen[7] reported that crown ethers could also be used to solubilize potassium permanganate in benzene, and Sam and Simmons[8] later observed that excellent yields could be obtained from the oxidation of organic compounds in these solutions. This method, although highly efficient, has not been widely applied, probably because of the rather high cost of crown ethers.

The work described in this report was originally designed to compare, under identical conditions, the usefulness of crown ethers and quaternary ammonium salts as phase transfer agents for permanganate oxidations. However, during the course of the study we were informed of work from Lehmkuhl's laboratory which indicated that dimethyl polyethylene glycols could also be used as phase transfer agents for potassium permanganate.[9] Consequently the scope of the study was enlarged to evaluate the usefulness of dimethyl polyethylene glycol in relationship to a typical quaternary ammonium ion phase transfer agent (Adogen 464) and a typical crown ether (dicyclohexano-18-crown-6) for the oxidation of alkenes.

The linear phase transfer agents (which Lehmkuhl called "Schleifenathers",[10] but which are also known as "glymes"[11]) consisted of a mixture of dimethyl polyethylene glycols with dimethyl octaethylene glycol as the principal component.[12] Previous work had shown that polyethers formed complexes with various cations,[13] and Lehmkuhl et al. have used them effectively as phase transfer agents for nucleophilic substitution reactions.[14]

In more recent studies (where these and other complexing

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