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Regiospecific Allenylation of Acetals with Propargyltrimethylsilanes Catalyzed by a Lewis Acid: Synthesis of α-Allenyl Ethers and 3-Silylated 3,4-Dihydrofurans

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Acetals easily undergo titanium tetrachloride or boron trifluoride etherate induced alkylation with simple and functional propargyltrimethylsilanes to lead to α-allenyl ethers in high yields. With alkyl α-substituted propargyltrimethylsilanes, 3-silylated 3,4-dihydrofurans may be also obtained.

Introduction

In principle, organomagnesium, -zinc, and -aluminum compounds prepared from propargylic halides should be useful reagents for the introduction of the allenyl group into diverse organic structures by standard organometallic methodology. In practice, this is not the case, since organometallics (Mg, Zn, Al) prepared from propargyl bromide react with electrophilic reagents to give, after hydrolysis, acetylenic derivatives chiefly, while those obtained from 2-bromo-1-butyne lead to a mixture of acetylenic and allenic derivatives (eq 1 and 2).[30]

$$\mathrm{HC{\equiv}CCH_2Br} \xrightarrow[\text{(2) R'COR''}]{\text{(1) M}} \mathrm{HC{\equiv}CCH_2C(OH)(R')(R'')} \qquad (1)$$

$$\begin{aligned}&\mathrm{CH_3C{\equiv}CCH_2Br} \xrightarrow[\text{(2) R'COR''}]{\text{(1) M}}\\ &\qquad \mathrm{CH_3C{\equiv}CCH_2C(OH)(R')(R'')} + \\ &\qquad \mathrm{CH_2{=}C{=}C(CH_3)C(OH)(R')(R'')} \qquad (2)\end{aligned}$$

Besides, with electrophilic reagents such as acetals, the reaction of magnesium and zinc compounds is very difficult and only aluminum derivatives give satisfactory results.[31,32]

In contrast, propargyltrimethylsilanes undergo catalyst-induced reactions with electrophiles, with regiospecific rearrangement (eq 3).[1-14]

$$\begin{aligned}&\mathrm{-C{\equiv}C\ddot{C}HSi(CH_3)_3} + \mathrm{E^+} \xrightarrow[\mathrm{CH_2Cl_2}]{\text{Lewis acid}}\\ &\qquad [\mathrm{(CH_3)_3Si\ddot{C}H\overset{+}{C}{=}\ddot{C}E}] \xrightarrow{\mathrm{Nu^-}}\\ &\qquad \mathrm{-CH{=}C{=}C(E){-}} + \mathrm{NuSi(CH_3)_3} \qquad (3)\end{aligned}$$

Attack at C-3 of the propargyl system generates a significant positive charge on the carbon atom β to the trimethylsilyl group; a stabilization due to σ–π conjugation[33] may be expected. Thus the positive charge will be delocalized onto the silicon atom. A further consequence of such σ–π conjugation will be a facile heterolysis[34] of the Si–C bond.

For instance, we have observed the results shown in eq 4.[1,7]

$$\begin{aligned}&\mathrm{RC{\equiv}CCH_2Si(CH_3)_3} + i\text{-}\mathrm{C_4H_9CH(OC_2H_5)_2} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{TiCl_4}}\\ &\qquad \mathrm{CH_2{=}C{=}C(R)CH(}i\text{-}\mathrm{C_4H_9)OC_2H_5} \qquad (4)\end{aligned}$$

$$\mathrm{R = H, yield\ 70\%;\ R = CH_3, yield\ 92\%}$$

In addition, propargyltrimethylsilanes show other advantages: they can be easily prepared with good yields, in many structural cases,[13] and they are air and moisture stable, while magnesium, zinc, and aluminum compounds are not.[35-37] Propargyltrimethylsilanes can be stored while magnesium, zinc, and aluminum derivatives must be used as soon as they have been prepared, since they undergo complicated and irreversible reactions at room temperature.[30,35-37]

In this paper, we describe the results obtained in the study of the reaction between various acetals and several propargyltrimethylsilanes, a number of them having other functionalities.

(1) Reaction of 1-(Trimethylsilyl)-2-butyne with Acetals in the Presence of Titanium Tetrachloride.

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Table I. $TiCl_4$-Induced Reaction of $CH_3C{\equiv}CCH_2Si(CH_3)_3$ with Acetals $(R')(R'')C(OR''')_2$

acetal			condtns[a]		
R′	R″	R‴	(2/1/2)	products	yield, %
i-C_4H_9	H	C_2H_5	a	$CH_2{=}C{=}C(CH_3)CH(i\text{-}C_4H_9)OC_2H_5$	92
H	H	n-C_4H_9	b	$CH_2{=}C{=}C(CH_3)CH_2O\text{-}n\text{-}C_4H_9$	96
CH_3	CH_3	CH_3	b	$CH_2{=}C(Cl)C(CH_3){=}C(CH_3)_2$	32
C_6H_5	H	CH_3	a	$CH_2{=}C{=}C(CH_3)CH(C_6H_5)OCH_3$ $CH_2{=}CClC(CH_3){=}CHC_6H_5$ (E + Z)	66 24
C_6H_5	H	CH_3	c	$CH_2{=}C{=}C(CH_3)CH(C_6H_5)OCH_3$	85
$CH_2{=}CHCH_2$	H	C_2H_5	b	$CH_2{=}C{=}C(CH_3)CH(CH_2CH{=}CH_2)OC_2H_5$	66
$HC{\equiv}CCH_2$	H	C_2H_5	b	$CH_2{=}C{=}C(CH_3)CH(CH_2C{\equiv}CH)OC_2H_5$	70
$ClCH_2$	H	n-C_4H_9	b	$CH_2{=}C{=}C(CH_3)CH(CH_2Cl)O\text{-}n\text{-}C_4H_9$	80

[a] mmol of acetal/mmol of $TiCl_4$/mmol of silane: (a) −78 °C, 10 min, −78 to −45 °C, 10 min; (b) −78 °C, 5 min, −78 to 0 °C, 20 min, 0 °C, 20 min; (c) −78 °C, 10 min.

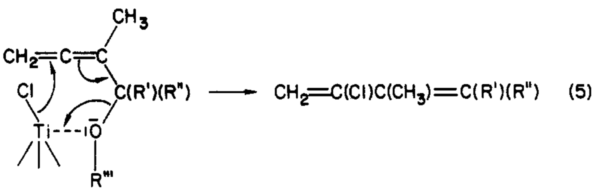
Table II. $TiCl_4$-Induced Reaction of Silanes $RC{\equiv}CCH_2Si(CH_3)_3$ with Acetals $R'CH(OR''')_2$

silane	acetal		condtns[a]		
R	R′	R‴	(2/1/2)	products	yield, %
H	i-C_4H_9	C_2H_5	a	$CH_2{=}C{=}CHCH(i\text{-}C_4H_9)OC_2H_5$	70
H	C_6H_5	CH_3	c	$CH_2{=}C{=}CHCH(C_6H_5)OCH_3$ $CH_2{=}CClCH{=}CHC_6H_5$ (E + Z)	46 10
n-C_4H_9	i-C_4H_9	C_2H_5	b	$CH_2{=}C{=}C(n\text{-}C_4H_9)CH(i\text{-}C_4H_9)OC_2H_5$	76
n-C_4H_9	C_6H_5	CH_3	b	$CH_2{=}C{=}C(n\text{-}C_4H_9)CH(C_6H_5)OCH_3$ $CH_2{=}CClC(n\text{-}C_4H_9){=}CHC_6H_5$ (E + Z)	59 10
n-C_4H_9	C_6H_5	CH_3	d	$CH_2{=}C{=}C(n\text{-}C_4H_9)CH(C_6H_5)OCH_3$	73
i-$C_3H_7CH(CH_3)$	i-C_4H_9	C_2H_5	b	$CH_2{=}C{=}C(i\text{-}C_3H_7CH(CH_3))CH(i\text{-}C_4H_9)OC_2H_5$	70
i-$C_3H_7CH(CH_3)$	C_6H_5	CH_3	b	$CH_2{=}C{=}C(i\text{-}C_3H_7CH(CH_3))CH(C_6H_5)OCH_3$	72
t-C_4H_9	i-C_4H_9	C_2H_5	b	$CH_2{=}C{=}C(t\text{-}C_4H_9)CH(i\text{-}C_4H_9)OC_2H_5$	20
t-C_4H_9	C_6H_5	CH_3	b	$CH_2{=}C{=}C(t\text{-}C_4H_9)CH(C_6H_5)OCH_3$ $CH_2{=}CClC(t\text{-}C_4H_9){=}CHC_6H_5$ (E + Z)	7 24
C_6H_5	i-C_4H_9	C_2H_5	b	$CH_2{=}C{=}C(C_6H_5)CH(i\text{-}C_4H_9)OC_2H_5$	47
C_6H_5	C_6H_5	CH_3	b	$CH_2{=}C{=}C(C_6H_5)CH(C_6H_5)OCH_3$	37
C_6H_5	C_6H_5	CH_3	e	$CH_2{=}CClC(C_6H_5){=}CHC_6H_5$ (E + Z)	32
CH_2OCH_3	i-C_4H_9	CH_3	b	$CH_2{=}C{=}C(CH_2OCH_3)CH(i\text{-}C_4H_9)OCH_3$	80
CH_2OCH_3	C_6H_5	CH_3	e	$CH_2{=}C{=}C(CH_2OCH_3)CH(C_6H_5)OCH_3$	51
CH_2OCH_3	$CH_2{=}CHCH_2$	C_2H_5	f	$CH_2{=}C{=}C(CH_2OCH_3)CH(CH_2CH{=}CH_2)OC_2H_5$	71
CH_2OH	i-C_4H_9	CH_3	f	$CH_2{=}C{=}C(CH_2OH)CH(i\text{-}C_4H_9)OCH_3$	<5
CH_2OH	i-C_4H_9	CH_3	f 5/4/4	$CH_2{=}C{=}C(CH_2OH)CH(i\text{-}C_4H_9)OCH_3$ $CH_2{=}CClC(CH_2OH){=}CH\text{-}i\text{-}C_4H_9$ (E + Z)	5 53
$CH_2OSi(CH_3)_3$	i-C_4H_9	CH_3	b	$CH_2{=}C{=}C(CH_2OH)CH(i\text{-}C_4H_9)OCH_3$	78
$CH_2OSi(CH_3)_3$	i-C_4H_9	CH_3	f	$CH_2{=}C{=}C(CH_2OH)CH(i\text{-}C_4H_9)OCH_3$	90
$CH_2OSi(CH_3)_3$	$CH_2{=}CHCH_2$	C_2H_5	f	$CH_2{=}C{=}C(CH_2OH)CH(CH_2CH{=}CH_2)OC_2H_5$	74

[a] mmol of acetal/mmol of $TiCl_4$/mmol of silane (see Table I for a–c): (d) −78 °C, 5 min, −78 to −50 °C, 5 min, −50 °C, 90 min; (e) −78 °C, 5 min, −78 to +20 °C, 20 min, 20 °C, 60 min; (f) −78 °C, 5 min, −78 to +15 °C, 10 min, 15 °C, 30 min.

Results summarized in Table I show that 1-(trimethylsilyl)-2-butyne is highly reactive toward saturated phenyl, allyl, propargyl, and α-functional acetals; the reaction always proceeds with propargylic rearrangement.

The expected α-allenyl ether may be accompanied by a chloroprenic derivative,[7,14] titanium tetrachloride acting as a chlorinating agent (eq 5). Such a derivative may be avoided if the temperature of the reaction is lowered.



Since this reaction, which appears sometimes with other propargyltrimethylsilanes (see the next paragraph), takes place when R′ = R″ = CH_3 and when R′ = H and R″ = C_6H_5, its driving force may be the decrease in the steric hindrance and the formation of a conjugated system particularly when a phenyl group is here.

(2) Reaction of 1-(Trimethylsilyl)-2-alkynes with Acetals in the Presence of Titanium Tetrachloride. The results in Table II show that the reaction of 1-(trimethylsilyl)-2-alkynes with acetals proceeds satisfactorily to afford the corresponding α-allenyl ethers, in good yield when R is a primary or secondary alkyl group or a phenyl group or has a functionality such as CH_2OCH_3 or $CH_2OSi(CH_3)_3$. Yields are lower when R is a tertiary alkyl group. The reaction also takes place with a propargylsilane vinylogue,[1] and, in this case, a double rearrangement occurs (eq 6).

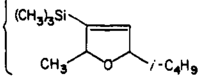
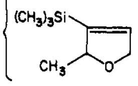
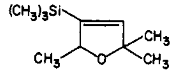
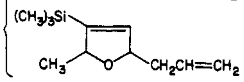
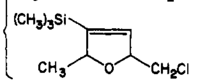
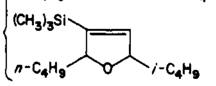
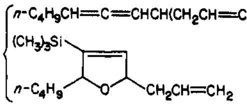
$$n\text{-}C_4H_9C{\equiv}CCH{=}CHCH_2Si(CH_3)_3 + R'CH(OR''')_2 \xrightarrow{\text{conditions (a)}} CH_2{=}CHCH{=}C{=}C(n\text{-}C_4H_9)CHR'OR''' \quad (6)$$

R′ = i-C_4H_9, R‴ = C_2H_5, yield 90%;
R′ = C_6H_5, R‴ = CH_3, yield 88%

Finally, chloroprenic derivatives may be obtained chiefly when the benzaldehyde dimethyl acetal is used as the electrophilic reagent.

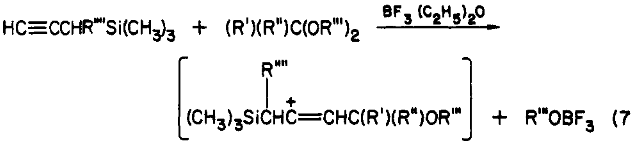
(3) Reaction of 3-(Trimethylsilyl)-1-alkynes Promoted by Boron Trifluoride Etherate. We have found that 3-(trimethylsilyl)-1-alkynes gave a mixture of products on reaction with acetals when $TiCl_4$ was the Lewis acid used, except when R = R'''' = H. Table III shows that α-allenyl ethers may be obtained if $BF_3{\cdot}O(C_2H_5)_2$ is used as a catalyst. However, in several cases, a 3-silylated

Table III. $BF_3{\cdot}O(C_2H_5)_2$-Induced Reaction of Silanes $HC{\equiv}CC(R)(R'''')Si(CH_3)_3$ with Acetals $(R')(R'')C(OR''')_2$

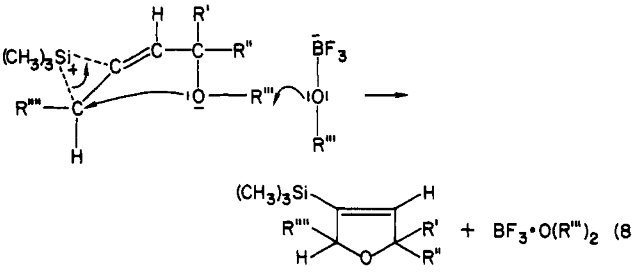
silane		acetal			condtns[a]		
R	R''''	R'	R''	R'''	(4/3/3)	products	yield, %
H	H	i-C_4H_9	H	C_2H_5	g	$CH_2{=}C{=}CHCH(i\text{-}C_4H_9)OC_2H_5$	65
CH_3	H	i-C_4H_9	H	C_2H_5	g	$CH_3CH{=}C{=}CHCH(i\text{-}C_4H_9)OC_2H_5$ 	45 38
CH_3	H	H	H	CH_3	g	$CH_3CH{=}C{=}CHCH_2OCH_3$ 	5 20
CH_3	H	CH_3	CH_3	CH_3	g		20
CH_3	H	$CH_2{=}CHCH_2$	H	C_2H_5	g	$CH_3CH{=}C{=}CHCH(CH_2CH{=}CH_2)OC_2H_5$ 	22 28
CH_3	H	$ClCH_2$	H	C_2H_5	g	$CH_3CH{=}C{=}CHCH(CH_2Cl)OC_2H_5$ 	21 22
n-C_4H_9	H	i-C_4H_9	H	C_2H_5	g	$n\text{-}C_4H_9CH{=}C{=}CHCH(i\text{-}C_4H_9)OC_2H_5$ 	48 39
n-C_4H_9	H	$CH_2{=}CHCH_2$	H	C_2H_5	g	$n\text{-}C_4H_9CH{=}C{=}CHCH(CH_2CH{=}CH_2)OC_2H_5$ 	23 32
C_6H_5	H	i-C_4H_9	H	C_2H_5	g	$C_6H_5CH{=}C{=}CHCH(i\text{-}C_4H_9)OC_2H_5$	95
C_6H_5	H	$CH_2{=}CHCH_2$	H	C_2H_5	g	$C_6H_5CH{=}C{=}CHCH(CH_2CH{=}CH_2)OC_2H_5$	80[b]
CH_3	CH_3	i-C_4H_9	H	C_2H_5	g	$(CH_3)_2C{=}C{=}CHCH(i\text{-}C_4H_9)OC_2H_5$	45

[a] mmol of acetal/mmol of $BF_3{\cdot}O(C_2H_5)_2$/mmol of silane: (g) −78 °C, 5 min, −78 to 0 °C, 5 min, 0 °C, 60 min. [b] Partial decomposition during distillation or in preparative GLC.

3,4-dihydrofuran is formed, via the possible cyclization of the intermediate under the influence of the boron trifluoride etherate (for similar cyclizations of allenic derivatives, see ref 15–17) (eq 7 and 8).



(7)



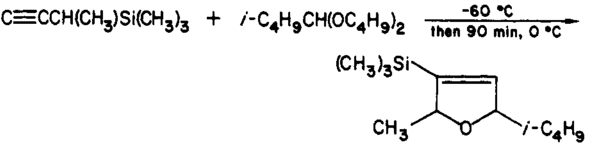
(8)

The reaction involves initial complexation of the acetal and boron trifluoride etherate to generate an alkoxy carbocation. Regiospecific electrophilic substitution of this cation at C-3 of the propargyltrimethylsilane provides a vinyl cation stabilized by interaction with the adjacent carbon–silicon bond. A 1,2-shift of the trimethylsilyl group[38,39] then affords an isomeric vinyl cation that is intercepted by the alkoxy group to produce a five-membered ring.

A similar rearrangement–cyclization type of mechanism is invoked in (trimethylsilyl)cyclopentene annulation,[40] with a migration of a trimethylsilyl group across the double bond of a vinyl cation.

The cyclization product (which does not occur when R'''' = C_6H_5 (Table III)) may be minimized, if the reaction is carried out at a lower temperature, but the yields of α-allenyl ethers are decreased as well.

On the other hand, we have observed that the 3,4-dihydrofuran formation can be maximized by using the following ratio: acetal/$BF_3{\cdot}O(C_2H_5)_2$/silane = 1/2/1 (eq 9).



(9)

yield 80%

However, such a cyclization does not occur with propargyltrimethylsilanes $RC{\equiv}CCH_2Si(CH_3)_3$ (R = alkyl), even with the above conditions.

Conclusion

Simple and functional propargyltrimethylsilanes undergo a catalyst-induced reaction with various acetals; an α-allenyl ether is generally obtained, in good yield. A chloroprenic derivative may be obtained as a byproduct when titanium tetrachloride is used as catalyst. With 3-(trimethylsilyl)-1-alkynes, a 3-silylated 3,4-dihydrofuran is observed in addition to α-allenyl ether when boron trifluoride etherate is used; a twofold ratio of this later reagent leads to pure 3-silylated 3,4-dihydrofuran, in good yield.

The formation of such silylated dihydrofurans is a synthetically interesting reaction, and further developments are intended.

Experimental Section

General Comments. All reactions were performed under an atmosphere of dry nitrogen or argon in flame-dried glassware. All solvents were rigorously dried before use. Infrared spectra were obtained by using a IR Beckman 4240 grating infrared spectrometer (absorption bands intensities: s, strong; vs, very strong; br, broad; m, medium; w, weak; vw, very weak). Proton NMR spectra were obtained by using a Perkin-Elmer R 24 A or a Bruker WM-250 spectrometer operating at 60 or 250 MHz, respectively. Proton chemical shifts are reported in δ units, parts per million downfield from internal tetramethylsilane; CCl_4 or $CDCl_3$ was used as solvent. Gas–liquid chromatography (GLC) was used extensively in this work in the analysis of reaction mixtures and isolation of pure products for analysis and spectroscopy. Commercial Intersmat IGC 12 M and 9OP3 Aerograph gas chromatographs were used. Analytic GLC columns were either a 6-ft SE-30 silicone rubber gum on Chromosorb P or a 6-ft Carbowax 20 M on Chromosorb W, and preparative GLC columns were 9-ft or 18-ft columns, with the same composition.

Preparation of Propargyltrimethylsilanes. The preparation of the following silanes has been previously described: $CH_3C{\equiv}CCH_2Si(CH_3)_3$;[13,18] $HC{\equiv}CCH_2Si(CH_3)_3$;[13,19] $n\text{-}C_4H_9C{\equiv}CCH_2Si(CH_3)_3$;[13] $(i\text{-}C_3H_7)(CH_3)CHC{\equiv}CCH_2Si(CH_3)_3$;[13] $t\text{-}C_4H_9C{\equiv}CCH_2Si(CH_3)_3$;[13] $C_6H_5C{\equiv}CCH_2Si(CH_3)_3$;[13] $HC{\equiv}CC(CH_3)_2Si(CH_3)_3$;[12] $HC{\equiv}CCH(CH_3)Si(CH_3)_3$;[18,20] $HC{\equiv}CCH(n\text{-}C_4H_9)Si(CH_3)_3$;[20,21] $HC{\equiv}CCH(C_6H_5)Si(CH_3)_3$.[20,21]

(4-Methoxy-2-butynyl)trimethylsilane.[22] To a stirred solution of 3-methoxy-1-propyne (5 g, 71 mmol) in 60 mL of THF was added a 1.6 M solution of *n*-butyllithium in hexane (45 mL, 71 mmol) while the temperature during the addition was maintained below −30 °C. The mixture was stirred at −30 °C for 15 min and at 0 °C for 15 min and then treated with (iodomethyl)trimethylsilane[23] (13.5 g, 63 mmol). The resultant solution was heated at 65 °C for 20 h. The cooled reaction mixture was poured into ice cold water. The aqueous phase was extracted with pentane (3 × 25 mL). The combined organic phases were dried over anhydrous $MgSO_4$. The organic layer was concentrated at reduced pressure. Distillation of the liquid residue gave 6.7 g (43 mmol, 68%) of (4-methoxy-2-butynyl)trimethylsilane: bp 83 °C (33 mmHg); $n^{20}{}_D$ 1.4429; IR (film) 2210 (s), 1250 (vs), 1090 (vs), 845 (br, vs) cm^{-1}; ^1H NMR (60 MHz) δ 0.12 (s, 9 H, $(CH_3)_3Si$), 1.45 (t, J = 2 Hz, 2 H, CH_2), 3.20 (s, 3 H, CH_3), 3.95 (t, J = 2 Hz, 2 H, OCH_2). Anal. Calcd for $C_8H_{16}OSi$: C, 61.48; H, 10.32. Found: C, 61.38; H, 10.36.

(4-Hydroxy-2-butynyl)trimethylsilane.[22] To a stirred 1.5 M solution of ethylmagnesium bromide in THF (77 mL, 120 mmol) was added propargyltrimethylsilane (11.2 g, 100 mmol) while the temperature was maintained at 20 °C. The mixture was stirred at 30 °C for 2 h, heated at 55 °C, and then treated with polyoxymethylene (6 g, 200 mmol). The resulting solution was stirred at 60 °C for 1 h, cooled, and subsequently hydrolyzed with 200 mL of saturated aqueous ammonium chloride. Workup as in the experiment above gave 6.5 g (46 mmol, 46%) of (4-hydroxy-2-butynyl)trimethylsilane: bp 70 °C (1 mmHg); IR (film) 3350 (br, vs), 2255 (w), 2220 (s), 1250 (vs), 1005 (s), 840 (br, vs) cm^{-1}; ^1H NMR (60 MHz) δ 0.10 (s, 9 H, $(CH_3)_3Si$), 1.45 (t, J = 2 Hz, 2 H, CH_2), 2.95 (s, 1 H, OH), 4.10 (t, J = 2 Hz, 2 H, OCH_2). Anal. Calcd for $C_7H_{14}OSi$: C, 59.10; H, 9.92. Found: C, 59.00; H, 9.95.

{4-[(Trimethylsilyl)oxy]-2-butynyl}trimethylsilane.[22] To a stirred solution of (4-hydroxy-2-butynyl)trimethylsilane (6.5 g, 46 mmol) and triethylamine (4.7 g, 46 mmol) in anhydrous diethyl ether (200 mL) was added trimethylchlorosilane (5 g, 46 mmol) while the temperature of the reaction was maintained at 0 °C. The white mixture was stirred during 4 h at room temperature and poured into water. Workup as in the experiment above gave 8.8 g (41 mmol, 90%) of {4-[(trimethylsilyl)oxy]-2-butynyl}trimethylsilane: bp 42 °C (0.05 mmHg); $n^{20}{}_D$ 1.4390; IR (film) 2260 (w), 2220 (s), 1250 (vs), 1065 (br, vs), 840 (br, vs) cm^{-1}; ^1H NMR (60 MHz) δ 0.12 (s, 18 H, $(CH_3)_3Si$), 1.45 (t, J = 2 Hz, 2 H, CH_2), 4.15 (t, J = 2 Hz, 2 H, OCH_2). Anal. Calcd for $C_{10}H_{22}OSi_2$: C, 56.00; H, 10.34. Found: C, 56.12; H, 10.30.

(2-Nonen-4-ynyl)trimethylsilane.[1] A solution of 45 mmol of (2-nonen-4-ynyl)lithium[24] in hexane–diethyl ether was treated with trimethylchlorosilane (4.9 g, 45 mmol) at 0 C. The mixture was stirred during 2 h at room temperature and subsequently hydrolyzed with 100 mL of saturated aqueous ammonium chloride. After usual workup, the organic layer was concentrated at reduced pressure. A trap-to-trap distillation afforded 6.1 g of a mixture of three (64:29:7) isomers. Pure samples were isolated from the distillate by preparative GLC (10-ft SE 30 on Chromosorb P, 145 °C). First eluted was 3-(trimethylsilyl)-1-nonen-4-yne: $n^{20}{}_D$ 1.4585; IR (film) 3085 (m), 3005 (m), 2235 (w), 1630 (s), 1250 (vs), 990 (s), 900 (s), 840 (br, vs) cm^{-1}; ^1H NMR (60 MHz) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.85 (t, 3 H, CH_3), 1.20–1.60 (m, 4 H, CH_2), 1.95–2.50 (m, 3 H, $CH_2C{\equiv}CCH$), 4.70–6.00 (m, 3 H, $CH_2{=}CH$). Second eluted was (2-nonen-4-ynyl)trimethylsilane (*Z* isomer): IR (film) 3020 (m), 2210 (w), 1605 (m), 1250 (vs), 840 (vs), 730 (m) cm^{-1}; ^1H NMR (60 MHz) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.90 (t, 3 H, CH_3), 1.30–1.60 (m, 4 H, CH_2), 1.70 (d, J = 8.2 Hz, 2 H, CH_2Si), 2.10–2.45 (m, 2 H, $CH_2C{\equiv}$), 5.15 (br d, J = 10 Hz, 1 H, $CH{=}$), 5.70 (dt, J = 10 Hz, J = 8.2 Hz, 1 H, ${=}CHCH_2$). Anal. Calcd for $C_{12}H_{22}Si$: C, 74.14; H, 11.41. Found: C, 74.08; H, 11.45. This second product was the silane used in our experiments. Third eluted was (2-nonen-4-ynyl)trimethylsilane (*E* isomer): IR (film) 3020 (m), 2220 (w), 1625 (m), 1250 (vs), 955 (s), 840 (br, vs) cm^{-1}; ^1H NMR (60 MHz) δ 0.00 (s, 9 H, $(CH_3)_3Si$), 0.90 (t, 3 H, CH_3), 1.25–1.60 (m, 4 H, CH_2), 1.47 (d, J = 8.2 Hz, 2 H, CH_2Si), 2.05–2.40 (m, 2 H, $CH_2C{\equiv}$), 5.10 (br d, J = 16 Hz, 1 H, $CH{=}$), 5.85 (dt, J = 16 Hz, J = 8.2 Hz, 1 H, ${=}CHCH_2$).

Preparation of Acetals. Several are commercial products; the others were prepared as follows:[25,26] $CH_2(OCH_3)_2$, bp 42 °C (760 mmHg), commercial product; $(CH_3)_2C(OCH_3)_2$, bp 80 °C (760 mmHg), commercial product; $C_6H_5CH(OCH_3)_2$, bp 88 °C (18 mmHg), commercial product; $ClCH_2CH(OC_2H_5)_2$, bp 158 °C (760 mmHg), commercial product; $CH_2(O\text{-}n\text{-}C_4H_9)_2$, bp 180 °C (760 mmHg), yield 77%; $i\text{-}C_4H_9CH(OCH_3)_2$, bp 62 °C (60 mmHg), yield 75%; $i\text{-}C_4H_9CH(OC_2H_5)_2$, bp 56 °C (18 mmHg), yield 85%; $i\text{-}C_4H_9CH(OC_4H_9)_2$, bp 110 °C (20 mmHg), yield 68%; $CH_2{=}CHCH_2CH(OC_2H_5)_2$, bp 44 °C (19 mmHg), yield 70%; $HC{\equiv}CCH_2CH(OC_2H_5)_2$, bp 78 °C (50 mmHg), yield 80%; $ClCH_2CH(O\text{-}n\text{-}C_4H_9)_2$, bp 108 °C (16 mmHg), yield 94% (acetal obtained from chloroacetaldehyde diethyl acetal by transetherification reaction).

Reaction of a Propargyltrimethylsilane with an Acetal in the Presence of Titanium Tetrachloride. The following general procedure was used. The reactions were carried out in a 50-mL three-necked flask equipped with a stirrer, a nitrogen inlet, a no-air stopper, and a low-temperature thermometer. A solution of the acetal (4 mmol) in dry dichloromethane (10 mL) was prepared under nitrogen and cooled to −78 °C, and 2 mmol (0.22 mL) of $TiCl_4$ was added by syringe. This mixture was stirred at −78 °C for 5 min; subsequently a propargylsilane (4 mmol) was added. The reaction mixture was stirred at the temperature and for the time indicated in Tables I and II and then hydrolyzed by the addition of 25 mL of saturated aqueous $NaHCO_3$. The aqueous phase was separated and extracted with three 30-mL portions of diethyl ether. The dried (K_2CO_3) organic layers were concentrated at reduced pressure, and the residue was trap-to-trap distilled into a liquid-nitrogen-cooled receiver. Pure samples were isolated by GLC (15% SE-30 on Chromosorb P).

Reaction of a Propargyltrimethylsilane with an Acetal in the Presence of Boron Trifluoride–Ethyl Etherate. The apparatus was the same as in the experiment described above. The following general procedure was used. A solution of the acetal (4 mmol) in dry dichloromethane (10 mL) was prepared under nitrogen and cooled to −78 °C. Boron trifluoride–ethyl etherate (3 mmol, 0.37 mL) was added by syringe. The resulting solution was stirred at −78 °C for 5 min, and a propargylsilane (3 mmol) was added. The reaction mixture was stirred at the temperature and for the time indicated in Table III. Subsequent workup followed the procedure described above. Pure samples were obtained by GLC.

Products Obtained by Reaction of Propargyltrimethylsilanes with Acetals. (1)-α-Allenyl Ethers. The following ethers obtained from $(CH_3)_2CHCH_2CH(OC_2H_5)_2$ were representative.

$CH_2{=}C{=}CHCH(OC_2H_5)CH_2CH(CH_3)_2$ in 70% yield from $(CH_3)_3SiCH_2C{\equiv}CH$: $n^{20}{}_D$ 1.4379; IR (film) 3060 (w), 1955 (s), 1090 (s), 840 (s) cm^{-1}; ^{1}H NMR (60 MHz) δ 0.90 (d, J = 5.8 Hz, 6 H, CH_3), 1.10 (t, J = 7 Hz, 3 H, OCH_2CH_3), 1.20–2.10 (m, 3 H, CH_2CH), 2.95–3.95 (m, 3 H, $CHOCH_2$), 4.50–5.20 (m, 3 H, $CH_2{=}C{=}CH$). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.95; H, 11.72.

$CH_2{=}C{=}C(CH_3)CH(OC_2H_5)CH_2CH(CH_3)_2$ in 92% yield from $(CH_3)_3SiCH_2C{\equiv}CCH_3$: $n^{20}{}_D$ 1.4432; IR (film) 3050 (w), 1960 (s), 1090 (s), 845 (s) cm^{-1}; ^{1}H NMR (60 MHz) δ 0.90 (d, J = 5.8 Hz, 6 H, CH_3), 1.10 (t, J = 7 Hz, 3 H, OCH_2CH_3), 1.12–1.90 (m, 6 H, CH_2CH, $CH_3C{=}$), 2.85–3.90 (m, 3 H, $CHOCH_2$), 4.40–4.70 (m, 2 H, $CH_2{=}$). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.45; H, 11.95.

$CH_2{=}CHCH{=}C{=}C(CH_2CH_2CH_2CH_3)CH(OC_2H_5)CH_2CH(CH_3)_2$ in 90% yield from $(CH_3)_3SiCH_2CH{=}CHC{\equiv}CCH_2CH_2CH_2CH_3$: $n^{20}{}_D$ 1.4740; IR (film) 3090 (m), 3060 (w), 1945 (s), 1615 (s), 1085 (s), 990 (s), 895 (s), 835 (w) cm^{-1}; ^{1}H NMR (60 MHz) δ 0.80–1.05 (m, 9 H, CH_3), 1.10 (t, J = 7 Hz, 3 H, OCH_2CH_3), 1.25–1.65 (m, 6 H, CH_2), 1.65–2.20 (m, 3 H, $CH_2C{=}$, CH), 2.95–3.60 (m, 2 H, OCH_2), 3.75 (t, 1 H, OCH), 4.75–5.30 (m, 2 H, $CH_2{=}$), 5.55–6.45 (m, 2 H, $CH{=}$). Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. Found: C, 81.37; H, 11.90.

$CH_3CH{=}C{=}CHCH(OC_2H_5)CH_2CH(CH_3)_2$ in 45% yield from $(CH_3)_3SiCH(CH_3)C{\equiv}CH$: $n^{20}{}_D$ 1.4426; IR (film) 1965 (s), 1085 (s), 870 (s) cm^{-1}; ^{1}H NMR (60 MHz) δ 0.90 (d, J = 5.8 Hz, 6 H, CH_3), 1.10 (t, J = 7 Hz, 3 H, OCH_2CH_3), 1.15–1.50 (m, 2 H, CH_2), 1.50–1.85 (m, 3 H, $CH_3CH{=}$), 1.85–2.20 (m, 1 H, CH), 3.00–3.90 (m, 3 H, CH_2OCH), 4.60–5.30 (m, 2 H, $CH{=}C{=}CH$). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.58; H, 11.96.

The following ethers were prepared and, the IR and ^{1}H NMR spectra of all these compounds, listed in the Tables I–III, showed the presence of the allenyl group.

(1) $CH_2{=}C{=}C(CH_3)CH_2O$-n-C_4H_9 in 96% yield from $CH_2(O$-n-$C_4H_9)_2$: $n^{20}{}_D$ 1.4443. Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.17; H, 11.48.

(2) $CH_2{=}C{=}C(CH_3)CH(C_6H_5)OCH_3$ in 85% yield from $C_6H_5CH(OCH_3)_2$: $n^{20}{}_D$ 1.5305. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.81; H, 8.07.

(3) $CH_2{=}C{=}C(CH_3)CH(CH_2CH{=}CH_2)OC_2H_5$ in 66% yield from $CH_2{=}CHCH_2CH(OC_2H_5)_2$: $n^{20}{}_D$ 1.4548. Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.60. Found: C, 79.02; H, 10.57.

(4) $CH_2{=}C{=}C(CH_3)CH(CH_2C{\equiv}CH)OC_2H_5$ in 70% yield from $HC{\equiv}CCH_2CH(OC_2H_5)_2$. Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.40. Found: C, 79.89; H, 9.42.

(5) $CH_2{=}C{=}C(CH_3)CH(CH_2Cl)O$-$n$-$C_4H_9$ in 80% yield from $ClCH_2CH(O$-n-$C_4H_9)_2$: $n^{20}{}_D$ 1.4622. Anal. Calcd for $C_{10}H_{17}OCl$: C, 63.65; H, 9.08; Cl, 18.79. Found: C, 63.72; H, 9.05; Cl, 18.71.

(6) $CH_2{=}C{=}CHCH(C_6H_5)OCH_3$ in 46% yield from $C_6H_5CH(OCH_3)_2$: $n^{20}{}_D$ 1.5350. Anal. Calcd for $C_{11}H_{12}O$: C, 82.47; H, 7.55. Found: C, 82.55; H, 7.51.

(7) $CH_2{=}C{=}C(n$-$C_4H_9)CH(i$-$C_4H_9)OC_2H_5$ in 76% yield from i-$C_4H_9CH(OC_2H_5)_2$: $n^{20}{}_D$ 1.4477. Anal. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found: C, 79.98; H, 12.42.

(8) $CH_2{=}C{=}C(n$-$C_4H_9)CH(C_6H_5)OCH_3$ in 73% yield from $C_6H_5CH(OCH_3)_2$: $n^{20}{}_D$ 1.5162. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.30. Found: C, 83.36; H, 9.33.

(9) $CH_2{=}C{=}C(i$-$C_3H_7CH(CH_3))CH(i$-$C_4H_9)OC_2H_5$ in 70% yield from i-$C_4H_9CH(OC_2H_5)_2$. Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.36; H, 12.55.

(10) $CH_2{=}C{=}C(i$-$C_3H_7CH(CH_3))CH(C_6H_5)OCH_3$ in 72% yield from $C_6H_5CH(OCH_3)_2$: $n^{20}{}_D$ 1.5138. Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.37; H, 9.65.

(11) $CH_2{=}C{=}C(t$-$C_4H_9)CH(i$-$C_4H_9)OC_2H_5$ in 20% yield from i-$C_4H_9CH(OC_2H_5)_2$. Anal. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found: C, 79.87; H, 12.49.

(12) $CH_2{=}C{=}C(t$-$C_4H_9)CH(C_6H_5)OCH_3$ in 7% yield from $C_6H_5CH(OCH_3)_2$. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.30. Found: C, 83.36; H, 9.28.

(13) $CH_2{=}C{=}C(C_6H_5)CH(i$-$C_4H_9)OC_2H_5$ in 47% yield from i-$C_4H_9CH(OC_2H_5)_2$: $n^{20}{}_D$ 1.5174. Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.49; H, 9.60.

(14) $CH_2{=}C{=}C(C_6H_5)CH(C_6H_5)OCH_3$ in 37% yield from $C_6H_5CH(OCH_3)_2$. Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.45; H, 6.80.

(15) $CH_2{=}C{=}C(CH_2OCH_3)CH(i$-$C_4H_9)OCH_3$ in 80% yield from i-$C_4H_9CH(OCH_3)_2$: $n^{20}{}_D$ 1.4512. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.60; H, 10.97.

(16) $CH_2{=}C{=}C(CH_2OCH_3)CH(C_6H_5)OCH_3$ in 51% yield from $C_6H_5CH(OCH_3)_2$. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.51; H, 7.88.

(17) $CH_2{=}C{=}C(CH_2OCH_3)CH(CH_2CH{=}CH_2)OC_2H_5$ in 71% yield from $CH_2{=}CHCH_2CH(OC_2H_5)_2$: $n^{20}{}_D$ 1.4652. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.50; H, 9.95. Found: C, 72.41; H, 9.98.

(18) $CH_2{=}C{=}C(CH_2OH)CH(i$-$C_4H_9)OCH_3$ in 90% yield from i-$C_4H_9CH(OCH_3)_2$: $n^{20}{}_D$ 1.4691. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.62; H, 10.64.

(19) $CH_2{=}C{=}C(CH_2OH)CH(CH_2CH{=}CH_2)OC_2H_5$ in 74% yield $CH_2{=}CHCH_2CH(OC_2H_5)_2$. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.46; H, 9.61.

(20) $CH_2{=}CHCH{=}C{=}C(n$-$C_4H_9)CH(C_6H_5)OCH_3$ in 88% yield from $C_6H_5CH(OCH_3)_2$: $n^{20}{}_D$ 1.5350. Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.32; H, 9.11.

(21) $CH_3CH{=}C{=}CHCH_2OCH_3$ in 5% yield from $CH_2(OCH_3)_2$. Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.26. Found: C, 73.50; H, 10.29.

(22) $CH_3CH{=}C{=}CHCH(CH_2CH{=}CH_2)OC_2H_5$ in 22% yield from $CH_2{=}CHCH_2CH(OC_2H_5)_2$. Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.60. Found: C, 78.98; H, 10.57.

(23) $CH_3CH{=}C{=}CHCH(CH_2Cl)OC_2H_5$ in 21% yield from $ClCH_2CH(OC_2H_5)_2$. Anal. Calcd for $C_8H_{13}OCl$: C, 59.81; H, 8.16; Cl, 22.07. Found: C, 59.75; H, 8.18; Cl, 22.01.

(24) n-$C_4H_9CH{=}C{=}CHCH(i$-$C_4H_9)OC_2H_5$ in 48% yield from i-$C_4H_9CH(OC_2H_5)_2$: $n^{20}{}_D$ 1.4492. Anal. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found: C, 79.85; H, 12.49.

(25) n-$C_4H_9CH{=}C{=}CHCH(CH_2CH{=}CH_2)OC_2H_5$ in 23% yield from $CH_2{=}CHCH_2CH(OC_2H_5)_2$. Anal. Calcd for $C_{13}H_{22}O$: C, 80.36; H, 11.41. Found: C, 80.46; H, 11.39.

(26) $C_6H_5CH{=}C{=}CHCH(i$-$C_4H_9)OC_2H_5$ in 95% yield from i-$C_4H_9CH(OC_2H_5)_2$: $n^{20}{}_D$ 1.5197. Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.50; H, 9.60.

(27) $C_6H_5CH{=}C{=}CHCH(CH_2CH{=}CH_2)OC_2H_5$ in 80% yield from $CH_2{=}CHCH_2CH(OC_2H_5)_2$. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.98; H, 8.50.

(28) $(CH_3)_2C{=}C{=}CHCH(i$-$C_4H_9)OC_2H_5$ in 45% yield from i-$C_4H_9CH(OC_2H_5)_2$: $n^{20}{}_D$ 1.4450. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.17. Found: C, 79.13; H, 12.14.

(2) Chloroprenic Derivatives. The chloroprenic derivative obtained from $(CH_3)_2C(OCH_3)_2$ was representative: $CH_2{=}C(Cl)C(CH_3){=}C(CH_3)_2$ in 32% yield from $(CH_3)_3SiCH_2C{\equiv}CCH_3$: $n^{20}{}_D$ 1.4647; IR (film) 3100 (w), 1650 (m), 1620 (s), 1595 (w), 875 (s) cm^{-1}; ^{1}H NMR (60 MHz) δ 1.70 (s, 3 H, CH_3), 1.75 (s, 6 H, $(CH_3)_2C{=}$), 4.90 and 5.20 (s, 1 H, $CH_2{=}$). Anal. Calcd for $C_7H_{11}Cl$: C, 64.37; H, 8.49; Cl, 27.14. Found: C, 64.30; H, 8.52; Cl, 27.10.

The following chloroprenic derivatives were obtained, and the IR and ^{1}H NMR spectra of all these compounds, listed in the Tables I and II, showed the presence of the dienyl group.

(1) $CH_2{=}C(Cl)C(CH_3){=}CHC_6H_5$ (E + Z) in 24% yield from $C_6H_5CH(OCH_3)_2$: $n^{20}{}_D$ 1.5652. Anal. Calcd for $C_{11}H_{11}Cl$: C, 73.95; H, 6.21; Cl, 19.84. Found: C, 73.85; H, 6.24; Cl, 19.78.

(2) $CH_2{=}C(Cl)CH{=}CHC_6H_5$ (E + Z) in 10% yield from $C_6H_5CH(OCH_3)_2$. Anal. Calcd for $C_{10}H_9Cl$: C, 72.96; H, 5.51; Cl, 21.53. Found: C, 72.86; H, 5.54; Cl, 21.45.

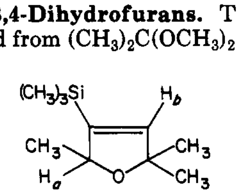
(3) $CH_2{=}C(Cl)C(n$-$C_4H_9){=}CHC_6H_5$ (E + Z) in 10% yield from $C_6H_5CH(OCH_3)_2$. Anal. Calcd for $C_{14}H_{17}Cl$: C, 76.18; H, 7.76; Cl, 16.06. Found: C, 76.09; H, 7.78; Cl, 15.98.

(4) $CH_2{=}C(Cl)C(t$-$C_4H_9){=}CHC_6H_5$ (E + Z) in 24% yield from $C_6H_5CH(OCH_3)_2$. Anal. Calcd for $C_{14}H_{17}Cl$: C, 76.18; H, 7.76; Cl, 16.06. Found: C, 76.21; H, 7.72; Cl, 15.95.

(5) $CH_2{=}C(Cl)C(C_6H_5){=}CHC_6H_5$ (E + Z) in 32% yield from $C_6H_5CH(OCH_3)_2$. Anal. Calcd for $C_{16}H_{13}Cl$: C, 79.83; H, 5.45; Cl, 14.72. Found: C, 79.91; H, 5.43; Cl, 14.69.

(6) $CH_2{=}C(Cl)C(CH_2OH){=}CH$-$i$-$C_4H_9$ (E + Z) in 53% yield from i-$C_4H_9CH(OCH_3)_2$. Anal. Calcd for $C_9H_{15}OCl$: C, 61.89; H, 8.65; Cl, 20.30. Found: C, 61.98; H, 8.62; Cl, 20.26.

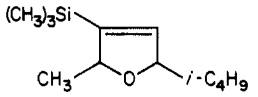
(3) 3-Silylated 3,4-Dihydrofurans. The following 3,4-dihydrofuran obtained from $(CH_3)_2C(OCH_3)_2$ was representative:



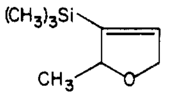
in 20% yield from $(CH_3)_3SiCH(CH_3)C{\equiv}CH$: IR (film) 3045 (m), 1600 (s), 1250 (vs), 1130 (s), 835 (vs) cm^{-1}; mass spectrum (inter alia), *m/e* (relative intensity) M^+ 184, $(CH_3)_3Si^+$ 73 (100); ^1H NMR (250 MHz) δ 0.12 (s, 9 H, $Si(CH_3)_3$), 1.17 (s, 3 H, CH_3), 1.21 (d, J = 6.5 Hz, 3 H, $CHCH_3$), 1.24 (s, 3 H, CH_3), 4.89 (dq, J = 6.5 Hz, J_{ab} = 2.25 Hz, 1 H, H_a), 5.87 (d, J_{ba} = 2.25 Hz, 1 H, H_b); ^{13}C NMR (62.8 MHz) δ 144.73, 142.46, 87.42, 85.19, 29.49, 27.60, 23.70, −1.11. Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.94. Found: C, 65.21; H, 10.90.

The measured spectra of this compound agreed with those reported in the case of 3,4-dihydrofurans[15,27] and vinylsilanes.[28]

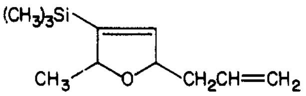
The following 3-silylated 3,4-dihydrofurans were obtained (Table III). Their IR, mass, ^1H NMR, and ^{13}C NMR spectra agreed with their structures.



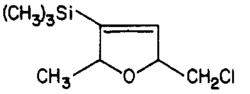
obtained in 38% yield from $i\text{-}C_4H_9CH(OC_2H_5)_2$: $n^{20}{}_D$ 1.4478. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.79; H, 11.37.



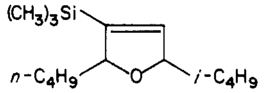
obtained in 20% yield from $CH_2(OCH_3)_2$. Anal. Calcd for $C_8H_{16}OSi$: C, 61.48; H, 10.32. Found: C, 61.55; H, 10.30.



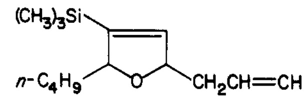
obtained in 28% yield from $CH_2{=}CHCH_2CH(OC_2H_5)_2$. Anal. Calcd for $C_{11}H_{20}OSi$: C, 67.28; H, 10.27. Found: C, 67.37; H, 10.24.



obtained in 22% yield from $ClCH_2CH(OC_2H_5)_2$. Anal. Calcd for $C_9H_{17}OClSi$: C, 52.79; H, 8.37; Cl, 17.33. Found: C, 52.86; H, 8.35; Cl, 17.28.



obtained in 39% yield from $i\text{-}C_4H_9CH(OC_2H_5)_2$: $n^{20}{}_D$ 1.4528. Anal. Calcd for $C_{15}H_{30}OSi$: C, 70.79; H, 11.88. Found: C, 70.71; H, 11.90.



obtained in 32% yield from $CH_2{=}CHCH_2CH(OC_2H_5)_2$: $n^{20}{}_D$ 1.4609. Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.58; H, 10.96.

Registry No. $CH_3C{\equiv}CCH_2Si(CH_3)_3$, 18825-29-1; $TiCl_4$, 7550-45-0; $(i\text{-}C_4H_9)CH(OC_2H_5)_2$, 3842-03-3; $H_2C(O\text{-}n\text{-}C_4H_9)_2$, 2568-90-3; $(CH_3)_2C(OCH_3)_2$, 77-76-9; $C_6H_5CH(OCH_3)_2$, 1125-88-8; $(CH_2{=}CHCH_2)CH(OC_2H_5)_2$, 10602-36-5; $(HC{\equiv}CCH_2)CH(OC_2H_5)_2$, 13397-78-9; $ClCH_2CH(O\text{-}n\text{-}C_4H_9)_2$, 17437-27-3; $CH_2{=}C{=}C(CH_3)CH(i\text{-}C_4H_9)OC_2H_5$, 77085-82-6; $CH_2{=}C{=}C(CH_3)CH_2O\text{-}n\text{-}C_4H_5$, 16356-10-8; $CH_2{=}C(Cl)C(CH_3){=}C(CH_3)_2$, 92544-35-9; $CH_2{=}C{=}C(CH_3)CH(C_6H_5)OCH_3$, 72014-31-4; ($E$)-$CH_2{=}C(Cl)C(CH_3){=}CHC_6H_5$, 78502-41-7; ($Z$)-$CH_2{=}C(Cl)C(CH_3){=}CHC_6H_5$, 78502-40-6; $CH_2{=}C{=}C(CH_3)CH(CH_2CH{=}CH_2)OC_2H_5$, 92544-36-0; $CH_2{=}C{=}C(CH_3)CH(CH_2C{\equiv}CH)OC_2H_5$, 92544-37-1; $CH_2{=}C{=}C(CH_3)CH(CH_2Cl)O\text{-}n\text{-}C_4H_9$, 92544-38-2; $HC{\equiv}CCH_2Si(CH_3)_3$, 13361-64-3; $(n\text{-}C_4H_9)C{\equiv}CCH_2Si(CH_3)_3$, 84140-28-3; $(i\text{-}C_3H_7)CH(CH_3)C{\equiv}CCH_2Si(CH_3)_3$, 92544-39-3; $(t\text{-}C_4H_9)C{\equiv}CCH_2Si(CH_3)_3$, 84140-30-7; $C(HC{\equiv}CCH_2Si(CH_3)_3$, 29578-46-9; $CH_3OCH_2C{\equiv}CCH_2Si(CH_3)_3$, 90933-83-8; $HOCH_2C{\equiv}CCH_2Si(CH_3)_3$, 90933-84-9; $(CH_3)_3SiOCH_2C{\equiv}CCH_2Si(CH_3)_3$, 90933-85-0; $(i\text{-}C_4H_9)CH(OCH_3)_2$, 57094-35-6; $CH_2{=}C{=}CHCH(C_6H_5)OCH_3$, 92544-40-6; ($E$)-$CH_2{=}CClCH{=}CHC_6H_5$, 92544-41-7; ($Z$)-$CH_2{=}CClCH{=}CH(C_6H_5$, 92544-42-8; $CH_2{=}C{=}C(n\text{-}C_4H_9)CH(i\text{-}C_4H_9)OC_2H_5$, 92544-43-9; $CH_2{=}C{=}C(n\text{-}C_4H_9)CH(C_6H_5)OCH_3$, 92544-44-0; ($E$)-$CH_2{=}CClC(n\text{-}C_4H_9){=}CHC_6H_5$, 92544-45-1; ($Z$)-$CH_2{=}CClC(n\text{-}C_4H_9){=}CHC_6H_5$, 92694-61-6; $CH_2{=}C{=}C(i\text{-}C_3H_7CH(CH_3))CH(i\text{-}C_4H_9)OC_2H_5$, 92544-46-2; CH_2<<drbC<<-drbC(i-$C_3H_7CH(CH_3))CH(C_6H_5)OCH_3$, 92544-47-3; $CH{=}C{=}C(t\text{-}C_4H_9)CH(i\text{-}C_4H_9)OC_2H_5$, 92544-48-4; $CH_2{=}C{=}C(t\text{-}C_4H_9)CH(C_6H_5)OCH_3$, 92544-49-5; ($E$)-$CH_2{=}CClC(t\text{-}C_4H_9){=}CHC_6H_5$, 92544-50-8; ($Z$)-$CH_2{=}CCl(t\text{-}C_4H_9){=}CHC_6H_5$, 92544-51-9; $CH_2{=}C{=}C(C_6H_5)CH(i\text{-}C_4H_9)OC_2H_5$, 92544-52-0; $CH_2{=}C{=}C(C_6H_5)CH(C_6H_5)OCH_3$, 92544-53-1; ($E$)-$CH_2{=}CClC(C_6H_5){=}CHC_6H_5$, 92544-54-2; ($Z$)-$CH_2{=}CClC(C_6H_5){=}CHC_6H_5$, 92694-62-7; $CH_2{=}C{=}C(CH_2CH_2OCH_3)CH(i\text{-}C_4H_9)OCH_3$, 92544-55-3; $CH_2{=}C{=}C(CH_2OCH_3)CH(C_6H_5)OCH_3$, 92544-56-4; $CH_2{=}C{=}C(CH_2OCH_3)CH(CH_2CH{=}CH_2)OC_2H_5$, 92544-57-5; $CH_2{=}C{=}C(CH_2OH)CH(i\text{-}C_4H_9)OCH_3$, 92544-58-6; ($E$)-$CH_2{=}CClC(CH_2OH){=}CH(i\text{-}C_4H_9)$, 92544-59-7; ($Z$)-$CH_2{=}CClC(CH_2OH){=}(i\text{-}C_4H_9)$, 92544-60-0; $CH_2{=}C{=}C(CH_2OH)CH(CH_2CH{=}CH_2)OC_2H_5$, 92544-61-1; $(n\text{-}C_4H_9){\equiv}CCH{=}CHCH_2Si(CH_3)_3$, 77085-79-1; $CH_2{=}CHCH{=}C{=}C(n\text{-}C_4H_9)CH(i\text{-}C_4H_9)OC_2H_5$, 77085-85-9; $CH_2{=}CHCH{=}C{=}C(n\text{-}C_4H_9)CH(C_6H_5)OCH_3$, 77085-86-0; $H_2C(OCH_3)_2$, 109-87-5; $ClCH_2CH(OC_2H_5)_2$, 621-62-5; $HC{\equiv}CCH(CH_3)Si(CH_3)_3$, 14583-73-4; $HC{\equiv}CCH(n\text{-}C_4H_9)Si(CH_3)_3$, 92544-62-2; $HC{\equiv}CCH(C_6H_5)Si(CH_3)_3$, 92544-63-3; $CH_3CH{=}C{=}CHCH(i\text{-}C_4H_9)OC_2H_5$, 92544-64-4; $CH_3CH{=}C{=}CHCH_2OCH_3$, 92544-66-6; $CH_3CH{=}C{=}CHCH(CH_2CH{=}CH_2)OC_2H_5$, 92544-68-8; $CH_3CH{=}C{=}CHCH(CH_2Cl)OC_2H_5$, 92544-70-2; $n\text{-}C_4H_9CH{=}C{=}CHCH(i\text{-}C_4H_9)OC_2H_5$, 92544-72-4; $n\text{-}C_4H_9CH{=}C{=}CHCH(CH_2CH{=}CH_2)OC_2H_5$, 92544-74-6; $C_6H_5CH{=}C{=}CHCH(i\text{-}C_4H_9)OC_2H_5$, 92544-75-7; $C_6H_5CH{=}C{=}CHCH(CH_2CH{=}CH_2)OC_2H_5$, 92544-76-8; $(CH_3)_2C{=}C{=}CHCH(i\text{-}C_4H_9)OC_2H_5$, 92544 77-9; $BF_3{\cdot}O(C_2H_5)_2$, 109-63-7; 2-methyl-3(trimethylsilyl)-5-isobutyl-2,5-dihydrofuran, 92544-65-5; 2-methyl-3-(trimethylsilyl)-2,5-dihydrofuran, 92544-67-7; 2,5,5-trimethyl-3-(trimethylsilyl)-2,5-dihydrofuran, 92575-14-9; 2-methyl-3-(trimethylsilyl)-5-allyl-2,5-dihydrofuran, 92544-69-9; 2-methyl-3-(trimethylsilyl)-5-(chloromethyl)-2,5-dihydrofuran, 92544-71-3; 2-butyl-3-(trimethylsilyl)-5-isobutyl-2,5-dihydrofuran, 92544-73-5; 2-butyl-3-(trimethylsilyl)-5-allyl-2,5-dihydrofuran, 92669-16-4; 3-methoxy-1-propyne, 627-41-8; (iodomethyl)trimethyl, 4206-67-1; (4-hydroxy-2-butynyl)trimethylsilane, 90933-84-9; ethyl bromide, 74-96-4; trimethylchlorosilane, 75-77-4; (2-nonen-4-ynyl) lithium, 67978-47-6; 3-(trimethylsilyl)-1-nonen-4-yne, 92544-78-0; (E)-(2-nonen-4-ynyl)trimethylsilane, 92544-80-4; (Z)-(2-nonen-4-ynyl)-trimethylsilane, 92544-79-1.

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