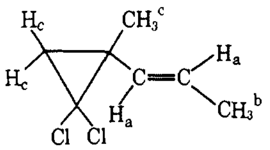
propylmethylcarbinol, which was isolated as a white solid after removal of solvents. Recrystallization from pentane, sublimation at 0.3 mm and room temperature, and recrystallization from pentane to a constant mp of 73–73.5° gave pure material: nmr ($CDCl_3$) δ 3.8 (m, 1 H, CH_3–C*H*–OH), 2.2 (s, 1 H, OH), 1.8–1.2 ppm (m, with two singlets and one doublet (J = 8 Hz) visible, 10 H); ir (CS_2) 3615 s, 3480 m, broad, 3000 sh, 2980 and 2965 s (doublet), 2935 s, 2875 m, 1390 sh, 1380 m, 1360 sh, 1325 w, 1255 s, 1235 w, 1165 s, 1135 s, 1110 s, 1095 sh, 1050 s, 1030 m, 1000 w, 980 s, 940 m, 890 s, 855 m, 830 s, 810 sh, and 730 m cm^{-1}; mass spectrum 45 (100) [$HOCHCH_3$], 67 (10) [C_5H_7], 103 (11) (M − ClC_2H_4O], 138 (8) [M − C_2H_4O], 182 (parent ion, not seen, as is usual for secondary and tertiary alcohols). *Anal.* Calcd for $C_7H_{12}OCl_2$: C, 45.92; H, 6.61; Cl, 38.73. Found: C, 45.61; H, 6.69; Cl, 38.34.

A by-product (14% yield) in this reaction was 1-(1-methyl-2,2-dichlorocyclopropyl)propene-1: nmr (CCl_4) δ 5.8 (m, 2 H_a), 2.1 (d, 3 H, J = 5 Hz, H_b), 1.75 ppm (m, 5H_c). *Anal.* Calcd for



$C_7H_{10}Cl_2$: C, 50.94; H, 6.11; Cl, 42.96. Found: C, 51.07; H, 6.60; Cl, 42.64. This product is derived from CCl_2 addition to 2-methyl-1,3-pentadiene. The latter most probably was formed by acid-catalyzed dehydration of the starting alcohol, the acid (HCl) arising from that portion of CCl_2 attack on the alcohol which occurs at the O–H bond.

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Addition of Grignard Reagents to Vinylsilanes

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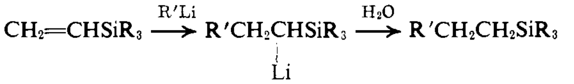
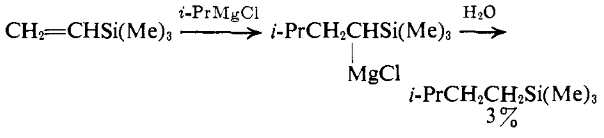
Abstract: The addition of Grignard reagents to vinylsilanes has been investigated with respect to the nature of the Grignard and to the substituents attached to the silicon atom. Alkoxy and chloro groups were found to exert an activating effect to the extent that quantitative yields of addition products frequently are observed. The structure of the Grignard reagent was found to have a pronounced effect, the order of reactivity being tertiary > secondary > primary.

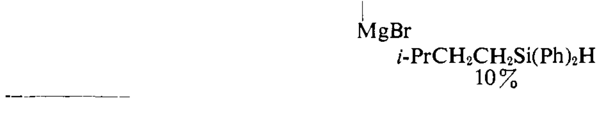
The addition of organolithium compounds to the double bond of vinylsilanes (eq 1) is well documented.[2–5] In contrast, the only report of an analogous addition reaction with Grignard reagents is between phenylmagnesium bromide and triethylperfluorovinylsilane.[4,5] Reinvestigation has shown that numerous Grignard reagents add to the vinyl group of vinylsilanes and that the extent of the reaction is sensitive to the substituents attached to the silicon atom (eq 2–4).



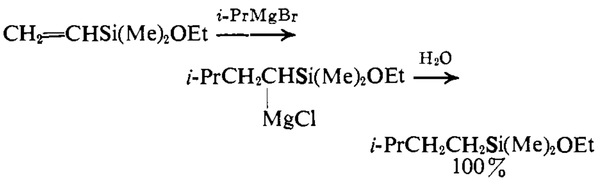
$$CH_2{=}CHSiR_3 \xrightarrow{R'Li} R'CH_2\underset{Li}{C}HSiR_3 \xrightarrow{H_2O} R'CH_2CH_2SiR_3 \quad (1)$$



$$CH_2{=}CHSi(Me)_3 \xrightarrow{i\text{-}PrMgCl} i\text{-}PrCH_2\underset{MgCl}{C}HSi(Me)_3 \xrightarrow{H_2O} \underset{3\%}{i\text{-}PrCH_2CH_2Si(Me)_3} \quad (2)$$



$$CH_2{=}CHSi(Ph)_2H \xrightarrow{i\text{-}PrMgBr} i\text{-}PrCH_2\underset{MgBr}{C}HSi(Ph)_2H \xrightarrow{H_2O} \underset{10\%}{i\text{-}PrCH_2CH_2Si(Ph)_2H} \quad (3)$$



$$CH_2{=}CHSi(Me)_2OEt \xrightarrow{i\text{-}PrMgBr} i\text{-}PrCH_2\underset{MgCl}{C}HSi(Me)_2OEt \xrightarrow{H_2O} \underset{100\%}{i\text{-}PrCH_2CH_2Si(Me)_2OEt} \quad (4)$$

When vinylsilanes containing labile groups on silicon (*e.g.*, chloro, alkoxy) are allowed to react with a Grignard reagent, one can envision two possible modes of reaction: (a) addition to the α- or β-carbon of the vinyl group, or (b) displacement of the labile group from the silicon atom (eq 5). Examination of the reaction mixtures have shown that the only major products originated from addition to the β-carbon of the vinyl group and displacement of the labile group from silicon. Authentic samples of the possible addition products were prepared by independent synthesis; the products of the reactions were separated and identified by comparison (nmr, ir, gc retention time) to the authentic samples. Indeed, groups such as alkoxy and halogen which normally are displaced by Grignard reagents activate the addition reaction to such an extent that the displacement reaction is often completely suppressed. This observation is in agreement with the activating

$$CH_2{=}CHSiR_{3-n}Y_n \xrightarrow{R'MgX} R'CH_2CH_2SiR_{3-n}Y_n + CH_3CHR'SiR_{3-n}Y_n + CH_2{=}CHSiR_{3-n}Y_{n-1}R' \quad (5)$$

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[1] (a) Aerospace Research Laboratories; (b) to whom correspondence should be addressed; (c) Faculte des Sciences.

[2] (a) L. F. Cason and H. G. Brooks, *J. Amer. Chem. Soc.*, **74**, 4582 (1952); (b) L. F. Cason and H. G. Brooks, *J. Org. Chem.*, **19**, 1278 (1954).

[3] D. Seyferth, T. Wada, and G. Raab, *Tetrahedron Lett.*, No. 22, 20 (1960).

[4] M. R. Stober, K. W. Michael, and J. L. Speier, *J. Org. Chem.*, **32**, 2740 (1967).

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Table I. Reactions of Grignard Reagents with Alkoxyvinylsilanes

Grignard	Vinylsilane	n	Addition, %	Substitution, %
i-PrMgCl	$CH_2{=}CHSiMe_{3-n}(OEt)_n$	0	3	0
		1	100	0
		2	100	0
		3	71	29
i-PrMgBr	$CH_2{=}CHSi(PhCH_2)_{3-n}(OMe)_n$			
$C_6H_{11}MgBr$		1	100	0
2-BuMgBr		2	100	0
tert-BuMgBr		3[a]		
i-PrMgBr	$CH_2{=}CHSi(Ph)_{3-n}(OMe)_n$	1	100	0
$C_6H_{11}MgBr$		2	100	0
2-BuMgBr		3[a]		

[a] A mixture of products was obtained, including $R''CH_2CH_2SiR_{3-n}(OMe)_{n-1}R''$.

Table II. Effect of Activating Groups upon the Addition of Grignard Reagents to Vinylsilanes

Reactant	RMgCl	X	Recovered reactant, %	Addition, % of product	Replacement, % of product	Addition + replacement
$CH_2{=}CHSiMe_2X$	i-Pr	-OEt	0	100	0	0
	i-Pr	-Cl	0	0	9	91
	1-Pr	-OEt	35	73	27	0
	1-Pr	-Cl	0	0	100	0
$CH_2{=}CHSi(CH_2Ph)_2X$	*tert*-Bu	-Cl	60	100	0	0
	i-Pr	-OMe	0	100	0	0
	i-Pr	-Cl	50	50	5	45
	1-Pr	-OMe	50	70	30	0
	1-Pr	-Cl	0	0	100	0
$CH_2{=}CHSi(Ph)_2X$	i-Pr	-OMe	0	100	0	0
	i-Pr	-Cl	66	40	Trace	60
	1-Pr	-OMe	53	20	80	0
	1-Pr	-Cl	0	0	100	0

effect of alkoxy groups found for other nucleophilic additions to vinylsilanes.[6]

Results

The addition of Grignard reagents to vinylsilanes has been studied with respect to the number of activating reactive substituents attached to the silicon atom (eq 6 and 7). Even though alkoxysilanes generally undergo

$$CH_2{=}CHSiMe_{3-n}(OEt)_n \xrightarrow{i\text{-PrMgCl}} i\text{-PrCH}_2CH_2Si(Me)_{3-n}(OEt)_n + CH_2{=}CHSiMe_{3-n}(OEt)_{n-1}\text{-}i\text{-Pr} \quad (6)$$

$$CH_2{=}CHSiR_{3-n}(OMe)_n \xrightarrow{R'MgBr} R'CH_2CH_2SiR_{3-n}(OMe)_n + CH_2{=}CHSiR_{3-n}(OMe)_{n-1}R' \quad (7)$$

$$R = Ph, PhCH_2$$

displacement reactions with organomagnesium compounds, only addition products were obtained when secondary and tertiary Grignard reagents were treated with mono- and dialkoxyvinylsilanes. When trialkoxyvinylsilanes were treated in a similar manner, mixtures of products were obtained (Table I).

Chloro groups have also been found to exert an activating effect on vinylsilanes, and a comparison of products obtained from the reaction of Grignard reagents with alkoxyvinylsilanes and chlorovinylsilanes (eq 8) is found in Table II. Since chlorosilanes are

$$CH_2{=}CHSiR_2X + R'MgCl \longrightarrow R'CH_2CH_2SiR_2X + CH_2{=}CHSiR_2R' + R'CH_2CH_2SiR_2R' \quad (8)$$

$$R = Me, Ph, PhCH_2;\ X = Cl, OEt, OMe$$

more reactive than the corresponding alkoxysilanes toward displacement reactions with Grignard reagents, it is not surprising that mixtures of products result from such reactions. Examples of both addition and displacement in the same molecule are common when secondary Grignard reagents are employed while normal Grignard reagents give displacement products exclusively. When *tert*-butylmagnesium chloride was allowed to react with chlorodibenzylvinylsilane, only the addition product was obtained, suggesting that the competition between addition and displacement reactions is sensitive to the steric requirements of the Grignard reagent.

Table III. Effect of the Structure of the Grignard Reagent on the Addition–Displacement Competition

Silane	R'MgX	Recovered silane	Addition, %	Displacement, %
$CH_2{=}CHSiMe_2OEt$	1-Pr	35	73	27
	1-Bu	10	66	34
	$PhCH_2$	48	0	100
	i-Pr	0	100	0
	2-Bu	0	100	0
	tert-Bu	10	100	0
$CH_2{=}CHSi(CH_2Ph)_2OMe$	1-Pr	50	70	30
	1-Bu	30	75	25
	$PhCH_2$	40	0	100
	i-Pr	0	100	0
	2-Bu	0	100	0
	c-Hex	0	100	0
	tert-Bu		100	0
$CH_2{=}CHSiPh_2OMe$	Me		0	100
	Et		0	100
	1-Pr	53	20	80
	1-Bu	30	22	75
	$PhCH_2$		0	100
	Ph		0	100
	Allyl		0	100
	i-Pr	0	100	0
	2-Bu	0	100	0
	c-Hex	0	100	0
	tert-Bu	100	0	0

The reactions of Grignard reagents with alkoxyvinylsilanes have been studied, with special emphasis placed on the structure of the Grignard reagent (Table III).

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(6) M. Prober, Abstracts, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1956, p 53-0.

Depending upon the specific reagent, results vary from 100% displacement to 100% addition. In these examples, all aliphatic secondary and tertiary Grignard reagents added to the vinyl group to the exclusion of the displacement route. Phenyl, benzyl, and allyl Grignards were found to afford only displacement products.

When the vinyl group is not attached directly to silicon, no addition is observed. Thus there was no reaction from the attempted addition of isopropylmagnesium chloride to allylethoxydimethylsilane; only displacement occurred when allyltriethoxysilane was treated with the same reagent (eq 9). Also, when the

$$CH_2{=}CHCH_2Si(OEt)_3 + i\text{-}PrMgCl \longrightarrow CH_2{=}CHCH_2Si(OEt)_2(i\text{-}Pr) \quad (9)$$

silicon atom of vinylsilanes is replaced by carbon, as in 1,1-dimethylallyl ethyl ether and chlorodimethylvinylmethane, no addition product was detected from their reaction with isopropylmagnesium chloride.

Discussion

The addition of Grignard reagents to vinyl groups usually occurs only in conjugated systems;[7] therefore, the ease with which these reagents add to vinylsilanes is surprising. Factors found to influence the addition reaction include: (a) the vinyl group must be bound to silicon; (b) the other groups which are bound to the silicon atom; (c) the steric requirements of the Grignard reagent.

It would be expected that the large +I effect of the trimethylsilyl group of trimethylvinylsilane would result in increased electron density in the ethylenic linkage and therefore it would be less susceptible to attack by the carbanion of a Grignard reagent than in the carbon analog. The opposite observation plus the finding that no addition occurs when a methylene group is inserted between the vinyl group and the silicon atom strongly suggests that reduced electron density (increased electrophilicity) at the vinyl double bond due to $d\pi$–$p\pi$ backbonding from the vinyl group to silicon is an important factor. Backbonding is considered to be an important factor in the chemistry of silicon[8,9] and there is spectral evidence for $d\pi$–$p\pi$ interaction between the vinyl and silicon of vinylsilanes.[10,11]

Alkoxy and chloro groups exhibit a dramatic activating effect upon the addition reaction, as might be expected since their −I effect would be expected to reduce the electron density at silicon, thereby increasing that atom's tendency to accept electron density from the vinyl group *via* backbonding. However, no correlation was found between the addition reaction and Taft substituent constants[12] for the groups bound to silicon.

The addition reaction has proven to be very sensitive to the nature of the Grignard reagent. The ratio of addition–displacement is roughly primary < secondary < tertiary, the same order found for the reactivity of Grignard reagents in their reactions with ketones[13] and for the steric requirements of the reagents. An exception is benzylmagnesium chloride, which reacts only by displacement although its reactivity is intermediate between secondary and tertiary Grignard reagents.[13]

In the competition between the addition and displacement reactions, steric considerations are more pronounced in the displacement attack at silicon, which presents a more sterically hindered center of attack than the vinyl group. For alkoxyvinylsilanes it is found that only primary Grignard reagents give appreciable amounts of the displacement product. In fact, no reaction was observed when isopropylmagnesium chloride was refluxed for 20 hr with (3-methylbutyl)ethoxydimethylsilane (the addition product of isopropylmagnesium chloride and ethoxydimethylvinylsilane). The more reactive chlorosilanes prefer the displacement route; however, the reaction of *tert*-butylmagnesium chloride with dibenzylchlorovinylsilane was found to proceed only with addition.

It is generally accepted that reaction of a Grignard reagent with an alkoxysilane proceeds by nucleophilic attack at silicon *via* either a square pyramidal or a trigonal bipyramidal pentacoordinate intermediate with coordination between the magnesium and the oxygen,[14–16] and the reaction usually occurs with retention of configuration at silicon. Most displacement reactions involving chlorosilanes proceed with inversion of configuration.[14,15] The pentacoordinate intermediate of this reaction is depicted as a trigonal bipyramid with the chlorine and the entering groups occupying the axial positions. Both of these intermediates would place the R group of the Grignard reagent in close proximity to a silicon bonded vinyl group, allowing either vinyl addition or displacement to occur from a common mechanistic path.

Investigations are currently being conducted to elucidate further the mechanism of these reactions. It is hoped that these experiments will identify and clarify the role of possible intermediates.

Experimental Section

Materials. All commercial chemicals were used without further purification unless otherwise noted. Grignard reagents were freshly prepared immediately prior to their use.

Analyses. Microanalyses were performed for The Aerospace Research Labs. by Galbraith Laboratories, Inc., Knoxville, Tenn.; those for the Laboratoire de Chimie Organique Physique were performed by Service Central de Micro-Analyse du CNRS, 94 Thiais.

General. Addition reactions were carried out under standard conditions of 16 hr under reflux, and the results are reported in Table IV. The reaction mixture was hydrolyzed with saturated ammonium chloride, filtered, and dried over anhydrous magnesium sulfate. After filtering, the products were quantitatively examined for products by gas chromatography. The reaction mixture was then rough distilled and samples for analyses were purified by means of preparative gas chromatography. New compounds were identified and characterized by elemental analyses and nmr. In the chlorodimethylvinylsilane series, the above procedure was employed; in other chlorovinylsilanes the products were distilled under vacuum directly from the reaction mixture. A typical example of the reaction procedure is given below.

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Table IV. Reactions of Grignard Reagents with Vinylsilanes

Silane	Grignard^b	Product	Calcd, % C	Calcd, % H	Calcd, % Si	Found, % C	Found, % H	Found, % Si	Bp (mm) or mp, °C
$CH_2{=}CHSiMe_2OEt$	PrMgCl	$1\text{-}PrCH_2CH_2SiMe_2OEt$	61.99	12.71	16.10	61.82	12.70	16.21	*a*
		$CH_2{=}CHSiMe_2(1\text{-}Pr)$	65.53	12.57	21.89	65.67	12.55	21.75	*a*
	BuMgCl	$1\text{-}BuCH_2CH_2SiMe_2OEt$	63.75	12.84	14.90	63.99	13.08	14.87	*a*
		$CH_2{=}CHSiMe_2(1\text{-}Bu)$	67.51	12.74	19.73	67.63	12.85	19.59	*a*
	$PhCH_2MgCl$	$CH_2{=}CHSiMe_2(CH_2Ph)$	74.92	9.14	15.92	75.07	9.22	16.01	*a*
	i-PrMgCl	$i\text{-}PrCH_2CH_2SiMe_2OEt$	62.00	12.72	16.11	62.21	12.84	15.88	*a*
	sec-BuMgCl	$2\text{-}BuCH_2CH_2SiMe_2OEt$	63.75	12.84	14.90	63.88	13.08	15.06	*a*
	tert-BuMgCl	$\mathit{tert}\text{-}BuCH_2CH_2SiMe_2OEt$	63.76	12.84	14.90	63.55	12.80	14.75	*a*
$CH_2{=}CHSi(CH_2Ph)_2OMe$	PrMgBr	$1\text{-}PrCH_2CH_2Si(CH_2Ph)_2OMe$	76.86	9.03	8.98	76.86	9.30	9.04	170 (12)
		$CH_2{=}CHSi(CH_2Ph)_2(1\text{-}Pr)$	81.36	8.62	10.01	81.56	8.48	10.50	165 (12)
	BuMgBr	$1\text{-}BuCH_2CH_2Si(CH_2Ph)_2OMe$	77.24	9.26	8.60	77.61	9.15	9.10	170–175 (12)
		$CH_2{=}CHSi(CH_2Ph)_2(1\text{-}Bu)$	81.57	8.90	9.54	81.48	8.90	9.10	170 (12)
	i-PrMgBr	$i\text{-}PrCH_2CH_2Si(CH_2Ph)_2OMe$	76.86	9.03	8.99	76.56	8.76	9.51	170 (12)
	sec-BuMgBr	$2\text{-}BuCH_2CH_2Si(CH_2Ph)_2OMe$	77.24	9.26	8.60	76.91	9.09	9.10	170–175 (12)
	$c\text{-}C_6H_{11}MgBr$	$C_6H_{11}CH_2CH_2Si(CH_2Ph)_2OMe$	78.35	9.15	7.97	78.64	9.18	7.55	
	tert-BuMgBr	$\mathit{tert}\text{-}BuCH_2CH_2Si(CH_2Ph)_2OMe$	77.24	9.26	8.60	77.51	9.30	8.90	
$CH_2{=}CHSiPh_2OMe$	MeMgBr	$CH_2{=}CHSiPh_2Me$	80.30	7.19	12.52	80.26	7.13	12.80	155 (12)
	EtMgBr	$CH_2{=}CHSiPh_2Et$	80.61	7.61	11.78	80.65	7.40	12.10	155 (12)
	PrMgBr	$1\text{-}PrCH_2CH_2SiPh_2OMe$	76.00	8.50	9.87	75.85	8.48	10.24	168 (12)
		$CH_2{=}CHSiPh_2(1\text{-}Pr)$	80.89	7.99	11.13	81.04	7.99	10.81	165 (12)
	BuMgBr	$1\text{-}BuCH_2CH_2SiPh_2OMe$	76.45	8.78	9.41	76.64	8.58	9.60	170 (12)
		$CH_2{=}CHSiPh_2(1\text{-}Bu)$	81.14	8.32	10.54	81.32	7.99	10.92	165 (12)
	$PhCH_2MgBr$	$CH_2{=}CHSiPh_2(CH_2Ph)$	83.94	6.71	9.35	84.25	6.55	9.60	
	$CH_2{=}CHCH_2MgBr$	$CH_2{=}CHSiPh_2(CH_2CH{=}CH_2)$	81.54	7.24	11.21	81.65	7.51	11.62	
	i-PrMgBr	$i\text{-}PrCH_2CH_2SiPh_2OMe$	76.00	8.50	9.87	75.89	8.64	10.08	165 (12)
	sec-BuMgBr	$2\text{-}BuCH_2CH_2SiPh_2OMe$	76.45	8.78	9.41	76.61	8.90	9.84	170 (12)
	$c\text{-}C_6H_{11}MgBr$	$C_6H_{11}CH_2CH_2SiPh_2OMe$	77.72	8.70	8.65	77.44	8.68	8.73	180 (12)
	$CH_2{=}CHMgBr$	$(CH_2{=}CH)_2SiPh_2$	81.30	6.82	11.88	81.16	6.76	12.04	160 (12)
	PhMgBr	$CH_2{=}CHSiPh_3$	83.86	6.33	9.80	83.73	6.19	9.70	65
$CH_2{=}CHSiMe_3$	*i*-PrMgCl	$i\text{-}PrCH_2CH_2SiMe_3$	66.57	13.96	19.45	66.87	14.06	19.44	*a*
$CH_2{=}CHSiMe(OEt)_2$	*i*-PrMgCl	$i\text{-}PrCH_2CH_2SiMe(OEt)_2$	58.76	11.84	13.74	59.04	11.97	13.97	*a*
$CH_2{=}CHSi(OEt)_3{}^c$	*i*-PrMgCl	$i\text{-}PrCH_2CH_2Si(OEt)_3$	56.36	11.18	11.98	56.58	11.13	12.19	*a*
		$CH_2{=}CHSi(OEt)_2(i\text{-}Pr)$	57.39	11.70	14.91	57.34	10.55	15.11	*a*
$CH_2{=}CHSi(OMe)_3{}^d$	*i*-PrMgBr	$CH_2{=}CHSi(OMe)_2(i\text{-}Pr)$	52.46	10.06	17.52	52.51	9.84	17.49	170 (760)
		$i\text{-}PrCH_2CH_2Si(OMe)_2(i\text{-}Pr)$	58.77	11.84	13.74	8.83	11.82	13.56	185 (760)
$CH_2{=}CHSiCH_2Ph(OMe)_2{}^e$	*i*-PrMgBr	$i\text{-}PrCH_2CH_2SiCH_2Ph(OMe)_2$	66.62	9.58	11.13	66.79	9.60	11.16	136 (12)
	$c\text{-}C_6H_{11}MgBr$	$C_6H_{11}CH_2CH_2SiCH_2Ph(OMe)_2$	69.81	9.64	9.60	70.06	9.47	9.76	160 (12)
	sec-BuMgBr	$2\text{-}BuCH_2CH_2SiCH_2Ph(OMe)_2$	67.62	9.84	10.54	67.65	9.92	10.50	148 (12)
$CH_2{=}CHSiPh(OMe)_2$	*i*-PrMgBr	$i\text{-}PrCH_2CH_2SiPh(OMe)_2$	65.50	9.30	11.78	66.23	9.17	11.60	130 (12)
	$c\text{-}C_6H_{11}MgBr$	$C_6H_{11}CH_2CH_2SiPh(OMe)_2$	69.01	9.41	10.09	69.10	9.44	10.30	146 (12)
	sec-BuMgBr	$2\text{-}BuCH_2CH_2SiPh(OMe)_2$	66.62	9.58	11.13	66.68	9.07	10.68	145 (12)
	t-BuMgBr	$\mathit{tert}\text{-}BuCH_2CH_2SiPh(OMe)_2$	66.62	9.58	11.13	66.72	9.41	10.55	150 (12)
$CH_2{=}CHSiMe_2Cl$	*i*-PrMgCl	$CH_2{=}CHSiMe_2(i\text{-}Pr)$	65.53	12.57	21.89	65.31	12.49	21.79	*a*
		$i\text{-}PrCH_2CH_2SiMe_2(i\text{-}Pr)$	69.67	14.03	16.29	69.98	13.91	16.17	*a*
$CH_2{=}CHSi(CH_2Ph)_2Cl$	*i*-PrMgBr	$CH_2{=}CHSi(CH_2Ph)_2(i\text{-}Pr)$	81.36	8.62	10.01	81.57	8.41	9.84	
		$i\text{-}PrCH_2CH_2Si(CH_2Ph)_2(i\text{-}Pr)$	73.39	8.95	7.80	73.50	8.85	8.10	
$CH_2{=}CHSiPh_2Cl$	*i*-PrMgBr	$i\text{-}PrCH_2CH_2SiPh_2(i\text{-}Pr)$	81.01	9.52	9.47	81.16	9.58	9.97	180 (12)
		$CH_2{=}CHSiPh_2(i\text{-}Pr)$	80.89	7.99	11.13	81.15	7.79	11.53	
$CH_2{=}CHSiPh_2H$	*i*-PrMgBr	$i\text{-}PrCH_2CH_2SiPh_2H$	80.24	8.71	11.03	80.13	8.96	11.27	
$CH_2{=}CHCH_2Si(OEt)_3$	*i*-PrMgCl	$CH_2{=}CHCH_2Si(OEt)_2(i\text{-}Pr)$	59.35	10.95	13.87	59.55	11.05	13.71	*a*

[a] Purified by gas chromatography. [b] The Grignard/silane ratio was 2:1 except where noted. [c] Grignard/silane = 1.1. [d] Grignard/silane = 4. [e] Grignard/silane = 3.

Reaction of Isopropylmagnesium Chloride with Ethoxydimethylvinylsilane. Isopropylmagnesium chloride was prepared from 19.6 g (0.25 mol) of isopropyl chloride and 6.1 g (0.25 g-atom) of magnesium. As rapidly as possible, there was added to the Grignard reagent 16.3 g (0.125 mol) of ethoxydimethylvinylsilane, and the mixture was stirred under reflux for 16 hr, after which a saturated solution of ammonium chloride was added dropwise until the salts coagulated. After removal of the salts by filtration, and drying over magnesium sulfate, the ether was removed by distillation and the reaction mixture was subjected to gas chromatographic analysis on a 150-ft × 0.01 in. DC-550 capillary column. The addition of 1 g of decane to the mixture allowed the integrated peak areas to be translated into amounts of material. After an analytical sample of the reaction product had been purified by gas chromatography on a 6 ft × 0.5 in. bi-wall column packed with 20% DC-550 on Chromosorb, comparison of the gas chromatographic response of the products with decane showed that the total yield was 21.4 g (98%) of ethoxydimethyl(3-methylbutyl)silane. Elemental analysis is reported in Table IV.

Table V. Preparation of Vinyl Compounds

Compd	Bp (lit.), °C	Yield, %
$CH_2{=}CHC(CH_3)_2Cl^e$	82 (79.5–80^a)	56
$CH_2{=}CHC(CH_3)_2OEt^e$	98–99 (98–99^b)	31
$CH_2{=}CHSi(CH_3)_2H$	37 (36.7 (738 mm^c))	73
$CH_2{=}CHSi(CH_3)_2Cl$	83–84 (82–82.5^c)	95
$CH_2{=}CHCHSi(CH_3)_2OEt$	122–124 (123–123.4^d)	92

[a] A. J. Ultree, *J. Chem. Soc.*, 530 (1948). [b] P. B. D. de la Marc and C. A. Vernon, *ibid.*, 2504 (1954). [c] J. W. Curry, *J. Amer. Chem. Soc.*, **78**, 1686 (1956). [d] L. D. Nasiak and H. W. Post, *J. Org. Chem.*, **24**, 849 (1959). [e] Gas chromatographic analysis indicates purity >98%.

Attempted Additions of Isopropylmagnesium Chloride to Vinylmethanes. No addition products were detected when isopropylmagnesium chloride was allowed to react with either 1,1-dimethylallyl ethyl ether or 1,1-dimethylallyl chloride under conditions identical with those employed for vinylsilane additions.

The following compounds were prepared for comparison purposes and/or for use as starting materials for vinyl additions: 3-methylbutyltrimethylsilane, 3-methylbutylethoxydimethylsilane, diphenylvinylsilane, 3-methylbutyldiphenylsilane. Syntheses were accomplished by the reaction of Grignard reagents and/or lithium aluminum hydride with the appropriate silanes. Standard methods were used in all instances and no unusual procedures were required for purification.

Cyclopropanol Derivatives as Intermediates for Organochemical Synthesis

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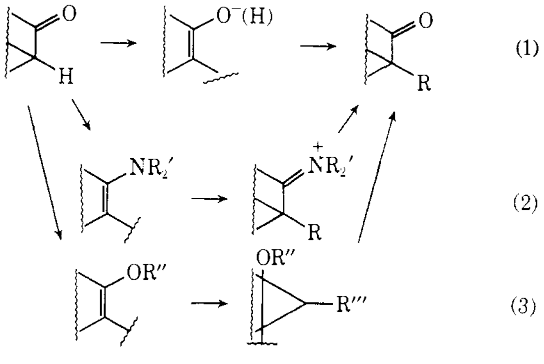
Abstract: A design of terpene synthesis based on the acid-induced transformations of cyclopropyl ethers and β-methoxycyclopropylcarbinols into quaternary α-methyl and α-vinyl carbonyl compounds, respectively, is described. Similar reactions with *gem*-dimethoxycyclopropanes are portrayed. A cyclopropylamine is shown to be inert. β-Methoxycyclopropanecarboxylic esters are converted into γ-ketocarboxylic acid derivatives. A similar ring unravelling of a β-acetoxycyclopropyl ketone is used for the synthesis of dihydrojasmone. An α-methoxycyclopropylcarbinol is transformed into a cyclobutanone on acid treatment and a mechanistically related cyclobutanone interconversion process is utilized for the construction of a bicyclic intermediate on route to the bourbonene sesquiterpenes.

The α-substitution of carbonyl compounds (*cf.* eq 1) has constituted the backbone of organochemical synthesis for many years. Despite the wide use of this carbon–carbon bond-forming process its limitations are being encountered with growing frequency as the complexity of structure of the substances in need of synthesis increases. Some of the resultant demand for alternate methods of synthesis have been met, *inter alia*, by the use of enamines (*cf.* eq 2),[2] but further flexibility in this area is desirable. The present communication describes a new procedure for α-alkylation of aldehydes and ketones *via* cyclopropyl ether and ester intermediates (*cf.* eq 3).



Broad advances in the chemistry of carbenes and carbenoid substances in the last two decades[3] have made cyclopropanation of olefins a facile process and cyclopropanes readily available materials. The fairly high reactivity of cyclopropanes, especially in ring cleavage reactions, has favored their use as intermediates in organochemical synthesis.[4] Our attention was drawn to the possible exploitation of cyclopropanols and their O-alkyl or O-acyl derivatives in synthesis by the exhaustive study of their chemistry by DePuy[5] and by our postulation of the intermediacy of cyclopropanediols in the Clemmensen reduction of β-diketones[6] and isolation of methoxycyclopropanes from a Clemmensen reduction of a vinylogous β-diketone.[7] As a consequence a study of the synthesis of alkoxy- and acyloxycyclopropanes and their protolysis was undertaken.

Methoxycyclopropanes. As first objective the construction of quaternary α-methylcarbonyl systems by way of unsymmetrically alkylated cyclopropyl ethers was investigated. Two model cyclopropanes, **4a** and **8a**, were chosen for this study. The former was prepared by consecutive transformations of 2,6-dimethylcyclohexanone (**1a**) into ketal **2**, acid-induced demethanolation,[8] and cyclopropanation of the resultant enol ether (**3a**) by the Simmons–Smith pro-

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(3) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

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