Vinyl-, Allyl-, and Phenylethynylsilanes. The Effect of Silicon on Their Reactions as Dienophiles and the Synthesis of Phenylated Phenyl- and Benzylsilanes

M. E. FREEBURGER AND LEONARD SPIALTER

Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio 45433

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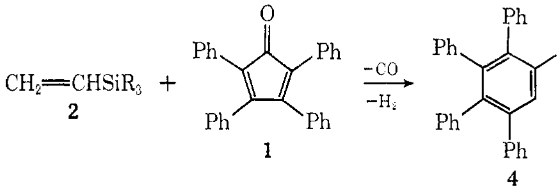
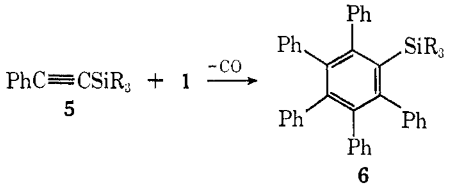
The Diels-Alder reaction of vinyl-, allyl-, and phenylethynylsilanes with tetraphenylcyclopentadienone was studied. In all cases, the reaction was slower than that of the carbon analogs. Allylsilanes gave the expected adducts, albeit slowly, but phenylethynylsilanes were generally unreactive, only phenylethynyltrimethylsilane affording an adduct. The reaction of vinylsilanes was complicated by the fact that the dihydrobenzene intermediate could lose either hydrogen or a silane moiety upon aromatization, resulting in a mixture of products. The product distribution was dependent upon solvent and the substituents on the silicon atom.

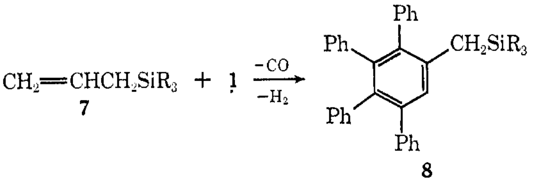
The Diels–Alder reaction of a variety of allyl-, ethynyl-, phenylethynyl-, and vinylsilanes with tetraphenylcyclopentadienone (tetracyclone) was investigated in order to (a) evaluate the effect of placing a silicon atom α or β to the dienophile, (b) synthesize moderately high molecular weight organosilicon compounds for evaluation as potential high temperature lubricant components,[1] and (c) prepare a series of silicon-containing monomers which could be incorporated into a Diels–Alder polymerization scheme.[2,3]

Tetraphenylcyclopentadienone (**1**) was chosen as the diene because it would provide adducts of moderately high molecular weight and because its versatility as a diene[4] and as a comonomer[2,3] in Diels–Alder reactions is well documented. The reaction of a vinylsilane (**2**) or ethynylsilane (**3**) with **1** afforded a 2,3,4,5-tetraphenylphenylsilane (**4**); a phenylethynylsilane (**5**) afforded a 2,3,4,5,6-pentaphenylphenylsilane (**6**); and an allylsilane (**7**) afforded a 2,3,4,5-tetraphenylbenzylsilane (**8**).



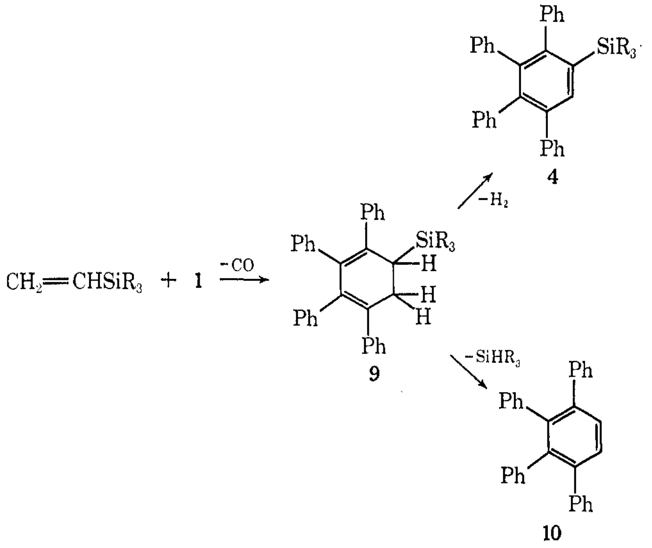
$$\underset{3}{HC\equiv CSiR_3} + 1 \xrightarrow{-CO} 4$$





Vinylsilanes.—The reaction of a vinylsilane with **1** is complicated by the fact that the intermediate dihydrobenzene (**9**) can aromatize in two ways, the loss of hydrogen to produce the phenylsilane **4** or the loss of a silane fragment to produce 1,2,3,4-tetraphenylbenzene (**10**) (Scheme I).

SCHEME I



Indeed, the loss of HX rather than H_2 in the aromatization is quite common when X does not contain carbon bonded directly to the dihydrobenzene ring.[4,5] When vinyltin compounds are condensed with **1**, only 1,2,3,4-tetraphenylbenzene and tin hydrides are obtained.[6–8]

In the condensation of a vinylsilane with **1**, both 1,2,3,-4-tetraphenylbenzene (**10**) and a 2,3,4,5-tetraphenylphenylsilane are formed. The ratio of these two products depends upon the solvent and the nature of the other substituents on the silicon atom. The possibility that the adducts had retained the carbonyl bridge or was a dihydrobenzene was ruled out by comparison of the infrared spectra of the adducts with that of 1,2,3,4-tetraphenylbenzene (Figure 1) and by the nmr of the adducts (Figure 2).

With vinyltrimethylsilane as the dienophile, the amounts of **10** and 2,3,4,5-tetraphenylphenyltrimethyl-

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[1] A. Adair and L. Spialter, patent applied for.

[2] J. K. Stille, F. W. Harris, R. O. Rakutis, and H. Mukamal, *J. Polym. Sci., Part B*, **4**, 791 (1966).

[3] J. K. Stille, R. O. Rakutis, H. Mukamal, and F. W. Harris, *Macromolecules*, **1**, 431 (1968).

[4] M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

[5] V. S. Abramov, *Bull. Acad. Sci. URSS, Classe Sci. Chim.*, 330 (1945); *Chem. Abstr.*, **40**, 5024 (1946).

[6] B. A. Arbuzov, L. A. Shapshinskaya, and M. I. Kudryavtseva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2160 (1961); *Chem. Abstr.*, **57**, 11223e (1962).

[7] L. A. Rothman and E. I. Becker, *J. Org. Chem.*, **24**, 294 (1959).

[8] L. A. Rothman and E. I. Becker, *ibid.*, **25**, 2203 (1960).

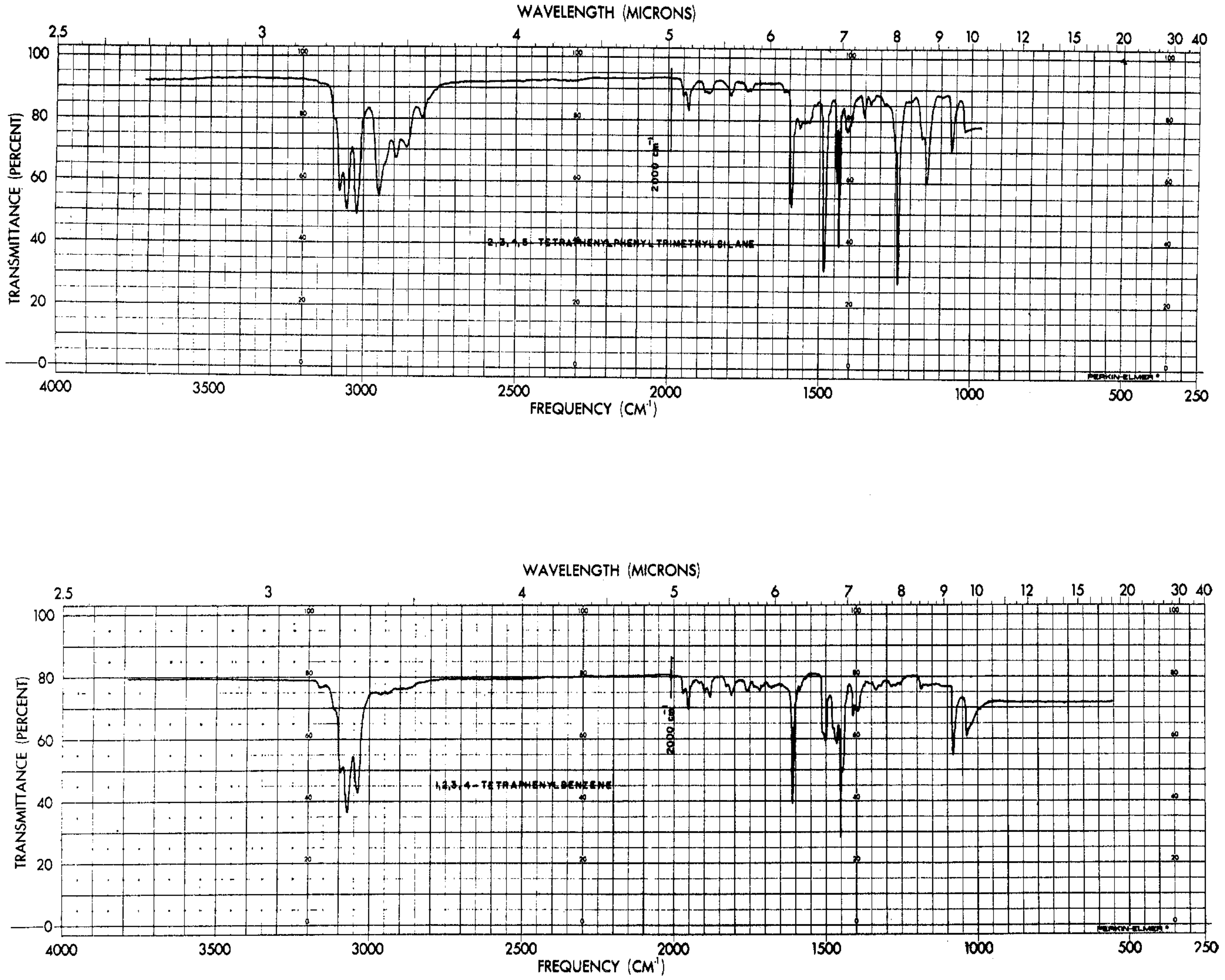


Figure 1.—Infrared spectra of 1,2,3,4-tetraphenylbenzene and 2,3,4,5-tetraphenylphenyltrimethylsilane.

silane (**11**) were determined in a variety of solvents (Table I). It was observed that only aromatic solvents yielded detectable amounts of **11**, with nitrobenzene affording an almost 1:1 mixture.

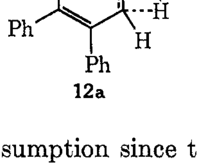
TABLE I.—THE EFFECT OF SOLVENT ON THE PRODUCT DISTRIBUTION OF THE REACTION OF VINYLTRIMETHYLSILANE WITH TETRAPHENYLCYCLOPENTADIENONE

Solvent	Total yield,[a] %	1,2,3,4-Tetraphenylbenzene (**10**),[b] %	2,3,4,5-Tetraphenylphenyltrimethylsilane (**11**),[b] %
Chloroform	78	100	0
n-Hexane	95	100	0
Tetrahydrofuran	26[c]	100	0
Benzene	95	75	25
Toluene	93	88	12
Toluene	90[d]	89	11
Toluene	90[e]	88	12
Nitrobenzene	*f*	74[g]	26[g]
Nitrobenzene	71[h]	54[h]	46[h]

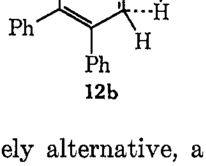
[a] All reactions were run for 24 hr at 200°, unless otherwise noted. The total yield is the amount of product isolated. [b] Percentages were determined by integration of the nmr spectrum (±3%) and are the relative amounts of each compound in the total yield. [c] Unreacted tetraphenylcyclopentadienone was present after 24 hr. [d] Run for 24 hr at 175°. [e] Run for 24 hr at 230°. [f] The last traces of nitrobenzene could not be removed without product loss. [g] This is a minimum figure for **11**; in the nmr analysis, residual nitrobenzene increases the calculated value of **10** and decreases that of **11**. [h] Isolated yields from a larger run.

For the series trimethyl-, dimethylethoxy-, methyldiethoxy-, and triethoxyvinylsilane, it was observed that the amount of silicon-containing product increased steadily with the increasing number of ethoxy groups (Table II).

The effect of solvent on the product distribution is difficult to rationalize. If one assumed a four-center transition state (**12a,b**) for the aromatization (a reasonable assumption since the likely alternative, a radical process, would predict polymerization of the olefin yet none was observed), then the argument could be made that an aromatic solvent stabilizes **12a** relative to **12b**. However, there is no direct proof that **12a** or **12b** exists and this is pure speculation. Changing the temperature did not effect the product distribution (see Table I).



12a



12b

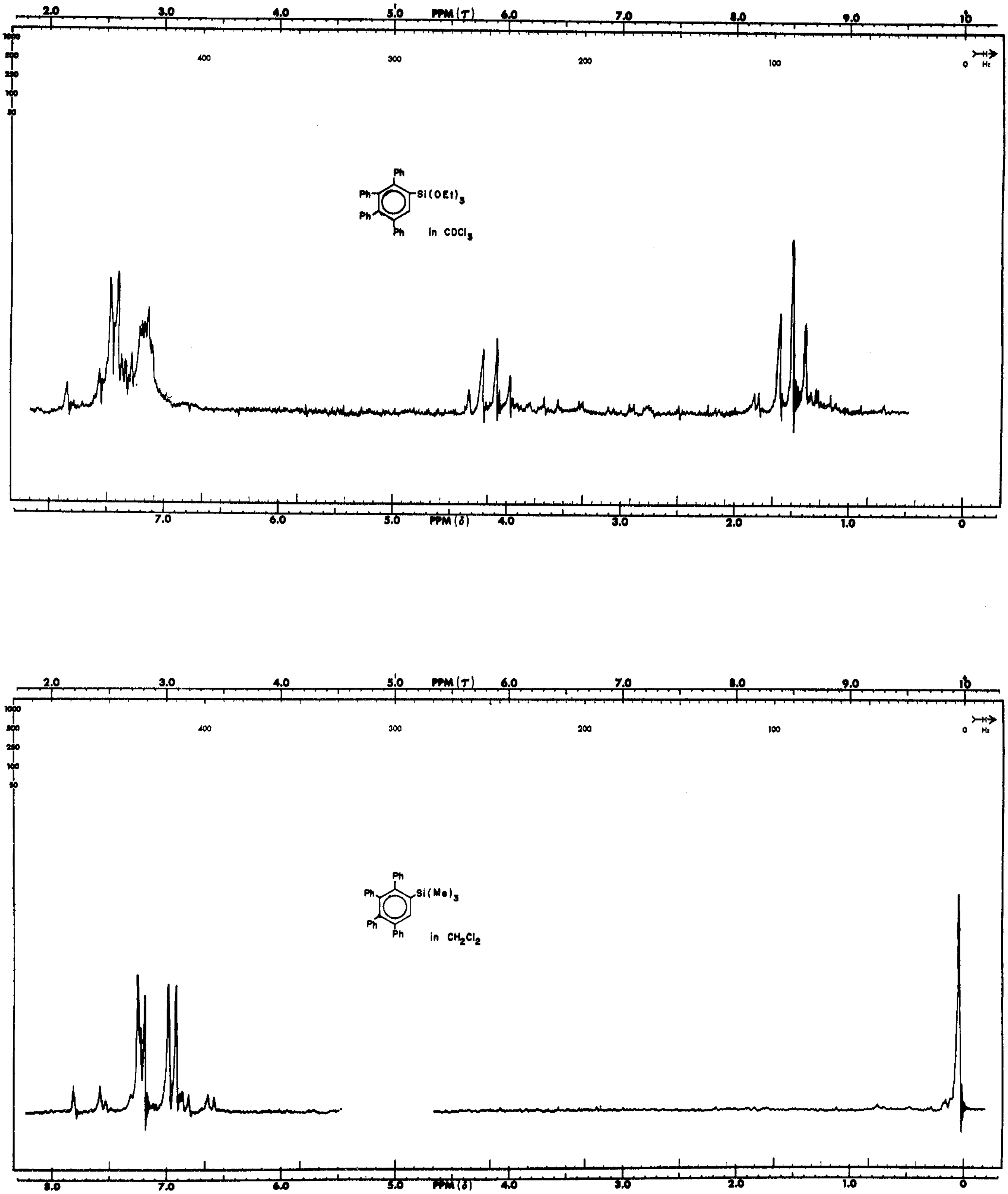


Figure 2.—60-MHz nmr spectra of 2,3,4,5-tetraphenylphenyltrimethylsilane and 2,3,4,5-tetraphenylphenyltriethoxysilane.

The substituents on silicon influence the strength of the bond between the dihydrobenzene ring and the silicon atom. Since a mixture of products is obtained, enough energy must be present to break either the C–H or C–Si bond and the difference in energy for loss of hydrogen or silane must be small. Any change which would increase the strength of the bond between silicon and the ring would favor retention of the silicon moiety.

Although a quantitative measure of the effect of substituents on the strength of the bond between the dihydrobenzene ring and silicon is impossible, qualitative estimates can be made. As the number of electronegative substituents on silicon is increased, the stretching frequency of the Si–C bond (and the Si–H bond) is shifted to higher frequency, indicating a strengthening of the bond.[9]

The Si–C stretching frequency, although not well investigated, occurs at about 800 cm^{-1} and is sensitive

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[9] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 2.

Table II.—The Effect of Substituents on Silicon on the Product Distribution of the Reaction of Vinylsilanes with Tetraphenylcyclopentadienone

Silane (CH_2=$CHSiR_1R_2R_3$)			Total yield,[a] %	1,2,3,4-Tetraphenylbenzene,[b] %	2,3,4,5-Tetraphenylphenylsilane,[b] %
R_1	R_2	R_3			
CH_3	CH_3	CH_3	93	88	12
CH_3	CH_3	OC_2H_5	90	78	22
CH_3	OC_2H_5	OC_2H_5	88	69	31
OC_2H_5	OC_2H_5	OC_2H_5	81	19	81
CH_3	CH_3	H	...[c]	100	0

[a] All reactions were run in toluene for 24 hr at 200°. The total yield is the amount of product isolated. [b] Percentages were determined by integration of the nmr spectrum (±3%) and are the relative amounts of each compound in the total yield. [c] Not determined.

Table III.—Infrared Stretching Frequencies of Si–C and Si–H Bonds in Substituted Silanes[10,11]

Compd	Si–C, cm^{-1}	Si–H, cm^{-1}
$(CH_3)_2(C_2H_5O)_2Si$	798	...
$CH_3(C_2H_5O)_3Si$	806	...
Allyl $(C_2H_5O)_3Si$	814	...
$(C_2H_5)_2(CH_3O)_2Si$	796	...
$C_2H_5(CH_3O)_3Si$	806	...
$C_2H_5(C_2H_5O)_3Si$	810	...
$(CH_3)_3SiH$	...	2118
$CH_3(C_2H_5O)_2SiH$	...	2165
$(C_2H_5O)_3SiH$	...	2196

Table IV.—Adducts from the Condensation of Allylsilanes and Tetraphenylcyclopentadienone[a]

Silane ($R_1R_2R_3R_4Si$)				Registry no.	Yield, %	Solvent	Temp, °C	Time, hr	Mp, °C	C		H		Si	
R_1	R_2	R_3	R_4							Found, %	Calcd, %	Found, %	Calcd, %	Found, %	Calcd, %
Allyl	CH_3	CH_3	CH_3	22931-61-9	76	Toluene	225	24	172.2–172.7	86.98	87.12	7.02	6.88	5.77	5.99
Allyl	CH_3	CH_3	C_6H_5	22931-62-0	96	Toluene	230	48	51	88.19	88.25	6.57	6.45	5.20	5.29
Allyl	OC_2H_5	OC_2H_5	OC_2H_5	22931-63-3	85	Toluene	200	48	Oil	79.35	79.52	6.66	6.85	4.83	5.02
Allyl	Allyl	C_6H_5	C_6H_5	22931-64-2	96	Toluene	230	48	118.7–119.8	91.48	91.31	6.03	5.79	3.01	2.88
Allyl	Allyl	OC_2H_5	OC_2H_5	22931-65-3	83	Benzene	200	96	103.2–104.6	86.82	87.18	6.06	6.20	3.34	3.08
Allyl	Allyl	Allyl	OC_2H_5	22931-66-4	97	Benzene	200	96	93.6–94.7	90.28	90.57	6.13	5.92	2.47	2.22
O-Allyl	O-Allyl	O-Allyl	O-Allyl	22931-67-5	75	Benzene	200	96	106.4–106.9	88.78	88.96	5.35	5.33	1.75	1.67

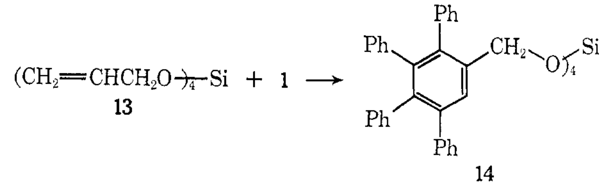
[a] The proton nmr spectra of all the adducts were consistent, both in appearance and integration, with the assigned structures.

to substitution on silicon, shifting to higher frequency with increased electronegative substitution.[10] The Si–H stretching frequency, which has received more investigation, shows a similar trend[11] (Table III).

The qualitative effect of increasing the number of electronegative groups on silicon is to increase the strength of the Si–C bonds (or Si–H bonds); this parallels the order observed for retaining the silicon moiety upon aromatization (Table II).

Allylsilanes.—Allylsilanes reacted cleanly with **1** to afford 2,3,4,5-tetraphenylbenzylsilanes in good yields. The reaction proceeds somewhat slower than that for the analogous carbon compounds,[4] although all the allylsilanes reacted completely after 24–48 hr at 230° or after 96 hr at 200°. Allyltriethoxysilane and diallyldiethoxysilane reacted completely with **1** in refluxing xylene after 7 and 14 days, respectively. In all cases the adducts had aromatized, as demonstrated by their infrared and nmr spectra.

The steric effects of the groups attached to the silicon atom appear to have little effect upon the condensation. Allyltriethoxysilane, diallyldiethoxysilane, and triallylethoxysilane afforded the mono-, di-, and triadducts in good yield. Tetraallyloxysilane (**13**) afforded the tetraadduct **14**.



A summary of the 2,3,4,5-tetraphenylbenzylsilanes prepared appears in Table IV.

Ethynylsilanes and Phenylethynylsilanes.—The reaction of ethynylsilanes with tetracyclone has been reported[12,13] and there is, of course, no problem of aromatization, since the adduct forms an aromatic system upon loss of carbon monoxide. Phenylethynylsilanes, however, are unreactive toward the condensation. This is evidently a result of the reenforcement of two retarding effects, electronic and steric.

The more electron rich the dienophile, the less reactive it is toward condensation with tetracyclone. Because of the electropositive character of silicon relative to carbon (+0.7 unit on the Pauling scale), the silyl group would be expected to exert a relatively strong inductive effect. Although the electronic effect of the triphenylsilyl group has not been investigated, the trimethylsilyl group has been shown to be an inductive electron donor.[14–16]

Because of the large inductive effect (relative to carbon), the silicon attached to the triple bond would be expected to retard the reaction (relative to carbon), and this is observed for the ethynylsilanes.[17,18] Disub-

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(10) R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 124 (1949).

(11) H. W. Thompson, *Spectrochim. Acta*, 238 (1960).

(12) D. Seyferth, C. Sarafidis, and A. Evnin, *J. Organometal. Chem.*, **2**, 417 (1964).

(13) C. S. Kraihanzel and M. L. Losee, *J. Org. Chem.*, **33**, 1983 (1968).

(14) J. L. Speier, *J. Amer. Chem. Soc.*, **75**, 2930 (1953).

(15) H. Freiser, M. V. Eagle, and J. Speier, *ibid.*, **75**, 2821 (1953).

(16) J. D. Roberts, E. A. McElhill, and R. Armstrong, *ibid.*, **71**, 2923 (1949).

(17) J. J. Dudkowski and E. I. Becker, *J. Org. Chem.*, **17**, 201 (1952).

(18) I. Benghiat and E. I. Becker, *ibid.*, **23**, 885 (1958).

stitution of the acetylene also increases the steric hindrance to the condensation.

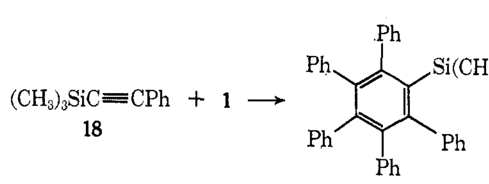
Neither phenylethynyltriphenylsilane (**15**), di(phenylethynyl)diphenylsilane (**16**), nor tri(phenylethynyl)phenylsilane (**17**) yielded an adduct after prolonged heating (72 hr, 315°) and some decomposition of the reactants was noted after this time. However, when the negative steric effects were somewhat alleviated by employing phenylethynyltrimethylsilane (**18**), a good yield of pentaphenylphenyltrimethylsilane (**19**) was obtained. Di(phenylethynyl) dimethylsilane (**20**) was not reactive.

$R_1R_2R_3SiPh + 1 \longrightarrow$ no reaction

15, $R_1 = R_2 = Ph; R_3 = PhC\equiv C$

16, $R_1 = Ph; R_2 = R_3 = PhC\equiv C$

17, $R_1 = R_2 = R_3 = PhC\equiv C$



18 **19**

$(CH_3)_2Si(C\equiv CPh)_2 + 1 \longrightarrow$ no reaction

20

In conclusion, vinylsilanes condense with tetracyclone, but the reaction is complicated by the choice of fragments which may be lost upon aromatization. The product distribution is effected by solvent and substitution on the silicon atom. Allylsilanes condense easily, affording the expected products in good yields, as do ethynylsilanes. Phenylethynylsilanes are, in general, unreactive. Evaluation of these compounds as potential lubricants and monomers is being conducted.

Experimental Section

The following compounds were obtained from the commercial sources indicated and used without further purification: diallyldiethoxysilane, triallylethoxysilane, tetraphenylcyclopentadienone (Aldrich Chemical Co.), trimethylvinylsilane, dimethylethoxyvinylsilane, triethoxyvinylsilane (Peninsular Chemresearch, Inc.), methyldiethoxysilane, allyltrimethylsilane, allyltriethoxysilane, diallyldiphenylsilane, and tetraallyloxysilane (Pierce Chemical Co.).

The proton nmr spectra were recorded on a Varian Associates A-60 spectrometer. Melting points were taken on a Mettler FP1 melting point apparatus and are uncorrected. The elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Vinyldimethylsilane.—To a slurry of 7.5 g (0.19 mol) of lithium aluminum hydride in *n*-butyl ether was added 100 g (0.77 mol) of vinyldimethylethoxysilane. The temperature was slowly raised to 120°, during which time the product distilled. The yield of vinyldimethylsilane, bp 37–38° (lit.[19] bp 36.7°), was 25 g (37%).

Allyldimethylphenylsilane.—Phenylmagnesium bromide was prepared by heating 31.8 g (0.20 mol) of bromobenzene and 4.8 g (0.20 g-atom) of magnesium in 150 ml of tetrahydrofuran (THF) at the reflux temperature for 2 hr. Following the dropwise addition of 27.0 g (0.20 mol) of dimethylallylchlorosilane, the mixture was kept at the reflux temperature for 18 hr. The reaction was quenched by addition of 100 ml of water, the organic layer was separated, and the THF was evaporated. The residue was dissolved in ether, washed twice with water, and dried over magnesium sulfate. Distillation of the residue yielded 35.2 g (88%) of allyldimethylphenylsilane, bp 44° (0.7 mm) [lit.[20] bp 90° (4 mm)].

Anal. Calcd for $C_{11}H_{16}Si$: C, 74.92; H, 9.15; Si, 15.93 Found: C, 75.08; H, 9.23; Si, 15.88.

Phenylethynyltriphenylsilane (**15**).—To a solution of 2.02 g (0.02 mol) of phenylacetylene and 100 ml of ether was added a commercial solution of *n*-butyllithium in *n*-hexane until the evolution of gas ceased. The mixture was then heated at reflux for 2 hr and 6.0 g (0.02 mol) of triphenylchlorosilane dissolved in 50 ml of ether was added. The reaction was heated at the reflux temperature for 3 days, 100 ml of 6% hydrochloric acid was added, and the ether layer was separated. After washings with aqueous sodium bicarbonate and drying over magnesium sulfate, the ether was evaporated and the residue was recrystallized from *n*-hexane. The yield of **15**, mp 94.3–94.6° (lit.[21] mp 100–101°), was 4.2 g (58%).

Anal. Calcd for $C_{26}H_{20}Si$: C, 86.62; H, 5.59; Si, 7.79. Found: C, 86.52; H, 5.62; Si, 7.62.

Di(phenylethynyl)diphenylsilane (**16**).—The same procedure used to prepare **15** was followed, except that diphenyldichlorosilane was employed. The yield of **16**, mp 79.3–79.6° (lit.[22] mp 80°), was 72%.

Anal. Calcd for $C_{28}H_{20}Si$: C, 87.45; H, 5.24; Si, 7.30. Found: C, 87.41; H, 5.21; Si, 7.42.

Tri(phenylethynyl)phenylsilane (**17**).—The same procedure used to prepare **15** was followed, except that phenyltrichlorosilane dissolved in benzene instead of ether was employed. The yield of **17**, mp 116.8–116.9°, was 50%.

Anal. Calcd for $C_{30}H_{20}Si$: C, 88.19; H, 4.93; Si, 6.87. Found: C, 88.19; H, 4.94; Si, 7.15.

Phenylethynyltrimethylsilane (**18**).—The same procedure used to prepare **15** was followed, except that trimethylchlorosilane was employed. The yield of **18**, bp 43° (0.05 mm) [lit.[23] bp 87.5–89.0° (9 mm)], was 75%.

Anal. Calcd for $C_{11}H_{14}Si$: C, 75.79; H, 8.10; Si, 16.11. Found: C, 75.91; H, 8.00; Si, 15.90.

Di(phenylethynyl)dimethylsilane (**20**).—The same procedure used to prepare **15** was followed, except that dimethyldichlorosilane was employed. The yield of **20**, mp 79.5–79.8°, was 61%.

Anal. Calcd for $C_{18}H_{16}Si$: C, 83.02; H, 6.19; Si, 10.78. Found: C, 83.20; H, 6.21; Si, 10.58.

Diels-Alder Adducts. General Procedure.—The silane, solvent, and tetraphenylcyclopentadienone were sealed in an evacuated glass tube and heated in a hydrogenation bomb for the time and at the temperature indicated. The tube was opened, the solvent and volatile silicon compounds were evaporated, and the residue was chromatographed on neutral alumina with *n*-hexane–chloroform (1:1). Most of the adducts solidified as brittle materials when the solvent was evaporated.

2,3,4,5-Tetraphenylbenzyltrimethylsilane.—The following procedure is typical for the condensations of the allylsilanes. A solution of 1.0 g (0.0025 mol) of tetracyclone and 0.30 g (0.0025 mol) of allyltrimethylsilane in 20 ml of toluene was heated at 225° for 24 hr in a sealed, evacuated glass tube. The tube was opened, the volatile materials were evaporated, and the residue was chromatographed, affording, after removal of the solvent, a white solid. The product was recrystallized from carbon tetrachloride. The yield of 2,3,4,5-tetraphenylbenzyltrimethylsilane, mp 172.2–172.7°, was 0.90 g (76%).

Pentaphenylphenyltrimethylsilane (**19**).—The following procedure is typical for the condensations of the phenylethynylsilanes. A solution of 0.77 g (0.002 mol) of tetraphenylcyclopentadienone and 0.34 g (0.002 mol) of phenylethynyltrimethylsilane in 10 ml of toluene was heated in a sealed, evacuated glass tube for 48 hr at 200°, after which time the purple color of **1** was still present. Additional heating at 225° for 48 hr dissipated the purple color. Evaporation of volatile materials and recrystallization of the residue from toluene afforded 0.99 g (93%) of **19**, mp 337–338°.

Anal. Calcd for $C_{39}H_{34}Si$: C, 88.25; H, 6.46; Si, 5.29. Found: C, 88.06; H, 6.46; Si, 5.50.

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(19) J. W. Curry, *J. Amer. Chem. Soc.*, **78**, 1686 (1956).

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(23) A. D. Petrov, L. L. Shchukovskaya, and Y. P. Egorov, *Dokl. Akad. Nauk SSSR*, **93**, 293 (1953); *Chem. Abstr.*, **48**, 13616 (1954).

Product Studies of Vinylsilane Condensations.—Tetracyclone (0.001 mol) and vinylsilane (0.0011 mol) were dissolved in 10 ml of solvent and heated in a sealed, evacuated tube. Volatile materials were removed by evaporation, the residue was dissolved in chloroform-*d*, and its nmr spectrum was recorded. Product distributions were obtained by the relative areas of the methyl and/or ethoxy signals and the total aromatic signal. Attempts to isolate pure products were not attempted unless there was a relatively high percentage of one component.

1,2,3,4-Tetraphenylbenzene.—Isolated from the reaction of trimethylvinylsilane with tetracyclone in toluene, this compound melted at 191.4° (lit.[24] mp 191°).

Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.79. Found: C, 94.04; H, 5.84.

2,3,4,5-Tetraphenylphenyltriethoxysilane.—Isolated from the reaction of triethoxyvinylsilane with tetracyclone in toluene, this yellow oil was purified by column chromatography.

Anal. Calcd for $C_{36}H_{36}SiO_3$: C, 79.37; H, 6.66; Si, 5.15. Found: C, 79.15; H, 6.74; Si, 5.36.

2,3,4,5-Tetraphenylphenyltrimethylsilane.—Isolated from the reaction of trimethylvinylsilane with tetracyclone in nitrobenzene, this compound melted at 193° (lit.[12] mp 200°).

Anal. Calcd for $C_{33}H_{30}Si$: C, 87.17; H, 6.65; Si, 6.17. Found: C, 86.90; H, 6.33; Si, 6.76.

Registry No.—**17**, 18866-47-2; **19**, 18856-11-6; **20**, 2170-08-3; 1,2,3,4-tetraphenylbenzene, 1487-12-3.

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Asymmetric Reduction. II. Preparation of Optically Active Benzyl-α-*d* Alcohol[1]

D. NASIPURI[2] AND C. K. GHOSH

Department of Chemistry, University College of Science,
92 Acharya P. C. Road, Calcutta-9, India

R. J. L. MARTIN

School of Chemistry, University of New South Wales, N. S. W. 2033, Australia

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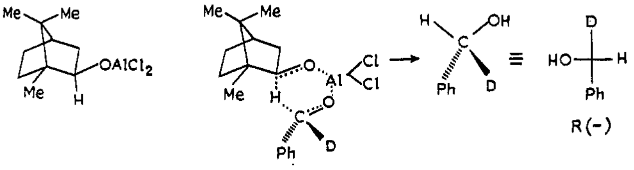
Optically active benzyl-α-*d* alcohol has been prepared by asymmetric reduction of benzaldehyde-1-*d* (or benzaldehyde) with six different reagents, namely, isobornyloxyaluminum dichloride, α-*d*-isobornyloxyaluminum dichloride, bornyloxyaluminum dichloride, isobornyloxymagnesium bromide, α-*d*-isobornyloxymagnesium bromide, and bornyloxymagnesium bromide. The extent of asymmetric induction is, respectively, 10.4, 17.8, 32.7, 52.2, 64.1, and 64.5%. The absolute configurations of benzyl-α-*d* alcohol from reduction with isoborneol complexes are in agreement with the preferred six-membered cyclic transition state where the bulky C-1 atom of the camphor nucleus and the phenyl group are oppositely placed, but the results of reduction with borneol complexes are anomalous. The extent of asymmetric reduction is greatly influenced by the reactivity of the reducing agent; the slower the rate, the greater the asymmetric induction.

In previous publications,[1,3,4] we have reported asymmetric reduction of a number of aliphatic and aromatic ketones with isobornyloxyaluminum dichloride[5] (**1**), a reagent easily prepared from commercially available (+)-camphor, lithium aluminum hydride, and anhydrous aluminum chloride.[6] The high asymmetric induction encountered in the reduction of aromatic ketones (the highest being 84% in the preparation of phenylisopropylcarbinol[4]) prompted us to examine its applicability in the preparation of optically active α-deuterated primary alcohols, *e.g.*, PhCHDOH, of known configuration, which are of importance for mechanistic and biochemical studies. Several reductions of this type involving hydride or deuteride transfer from optically active reagents to aliphatic or aromatic aldehydes are already known.[7-9] The general principle of these reactions is exemplified in the reduction of benzaldehyde-1-*d* with isobornyloxyaluminum dichloride (**1**) as shown below.



1 **2** **3**

On the basis of the usually accepted six-membered cyclic transition state for these reactions,[10] the preferred transition state is the one (**2**) where the bulkier C_1–Me side of the camphor nucleus and phenyl group are oppositely placed in the quasi-six-membered ring.[11] The preponderant enantiomer of the deuteriobenzyl alcohol that results from the reaction will therefore have the *R* configuration (**3**), which is levorotatory.[12] Six such asymmetric reductions, including the one described above, have now been carried out with reagents derived from (−)-isoborneol and (−)-borneol, all leading to optically active benzyl-α-*d* alcohol. The results are summarized in Table I, along with some earlier data from the literature.

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