

added 2-phenylbutyric anhydride (4 mmol) and the mixture was maintained at room temperature for 18 hr. To this mixture was added 2 ml of water and 2 ml of benzene. After 1 hr, the excess of acid was titrated with 1.0 *M* sodium hydroxide (phenolphthalein). The results indicated that only 40% of esterification had occurred. The slightly alkaline solution was extracted with chloroform (four 15-ml portions) and the extracts were discarded. The aqueous layer was acidified with concentrated hydrochloric acid and extracted with benzene (three 20-ml portions). The benzene extract was washed twice with brine, dried, evaporated, and sublimed, providing (-)-2-phenylbutyric acid, $[\alpha]^{25}_D -1.5^\circ$ (*c* 25, CCl_4). (+)-2-Phenylbutyric acid, obtained by the hydrolysis of the 3-thujopsanol 2-phenylbutyrate with aqueous

alcoholic potassium hydroxide for 24 hr at reflux, exhibited $[\alpha]^{25}_D +3^\circ$ (*c* 25, CCl_4).

Registry No.—2, 25966-77-2; 2 *p*-nitrobenzoate, 25966-78-3; 3, 25966-79-4; 4, 26039-33-8; 4 *p*-nitrobenzoate, 25966-80-7; 5, 25966-81-8; 8, 25966-82-9; 8 *p*-nitrobenzoate, 25966-83-0; 11, 25966-84-1.

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Addition of Silicon Hydrides to Olefinic Double Bonds. XII. Use of Aminosilicon Hydrides and Silazane Hydrides

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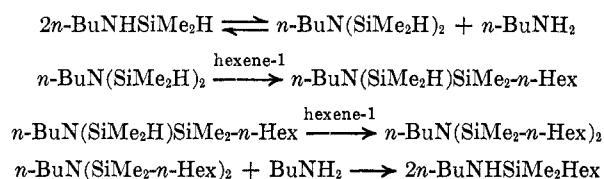
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The addition of aminosilicon hydrides and silazane hydrides to olefins and to dimethylaminodimethylvinylsilane in the presence of chloroplatinic acid was studied. *n*-Butylaminodimethylsilane and hexene-1 formed 2-*n*-butyl-1-*n*-hexyl-1,1,3,3-tetramethyldisilazane which diminished as the reaction proceeded to form *n*-butylamino-hexyldimethylsilane. Dialkylaminodimethylsilanes and trisdimethylaminosilane reacted very little, if at all, with olefins. *sym*-Tetramethyldisilazane behaved much like *sym*-tetramethyldisiloxane in having similar reactivity and in forming *sec*-alkyl adducts from pentene-2. Dimethylaminodimethylsilane added to hexene-1 smoothly in the presence of *sym*-tetramethyldisilazane, but not in its absence. Methyl methacrylate, methyl acrylate, allyl chloride, methallyl chloride, or allyl acetate each gave complex mixtures of many products with *sym*-tetramethyldisilazane. Allylamine gave hydrogen. Trisdimethylsilylamine formed the dihexyl adduct, no trihexyl adduct, and products that indicated redistribution of methyl groups and hydrogen on the silicon atoms during the reaction. Poly-*N*-allylmethylsilazane reacted to form a polymer which degraded in methanol to form 2-(dimethoxymethylsilyl)propylamine.

More than 2000 examples of the addition of siloxane, and of halo- or alkoxy-, aryl-, and alkylsilicon hydrides to olefins with platinum catalysts have been described.¹ However, the only report of an aminosilicon hydride adding to an olefin is that of *sym*-tetramethyldisilazane adding to tertiary allyl amines.² Chemical and physical data indicate that Si-N bonds of disilazanes and trisilylamines are different from those of monosilylated amines.³⁻⁵ We wished to determine the effect of structure among silicon hydrides that were aminosilanes, silazanes, and trisilylamines on their addition to olefins with chloroplatinic acid as a catalyst. To do this a series of hydrides was prepared. The series included *n*-butylaminodimethylsilane (*n*-BuNHSiMe₂H), anilindimethylsilane (PhNHSiMe₂H), dialkylaminodimethylsilanes (R₂NMe₂SiH, R = Me, Et, *n*-Bu), trisdimethylaminosilane [(Me₂N)₃SiH], *sym*-tetramethyldisilazane [HN(SiMe₂H)₂], *sym*-diphenyldimethyldisilazane [HN(SiMePhH)₂], and trisdimethylsilylamine [N(SiMe₂H)₃]. Chloroplatinic acid in propanol-2 was used as a catalyst with hexene-1 or pentene-1 and pentene-2 as typical olefins. Other unsaturated compounds were also used including poly-*N*-allylmethylsilazane [CH₂=CHCH₂-N(SiHMe)₂]_{*n*}, allylamine, and other allyl or methallyl compounds.

Results and Discussion

n-Butylaminodimethylsilane with hexene-1 and chloroplatinic acid at 100° reacted smoothly but followed an unexpected course. After 1 hr the chief products were 2-*n*-butyl-1-*n*-hexyl-1,1,3,3-tetramethyldisilazane and butylamine. After 3 hr the disilazane had been largely converted to *n*-butylamino-hexyldimethylsilane. Formation of these products probably occurred by a sequence of reactions as in the following reactions.



Anilindimethylsilane under the same conditions formed a 96% yield of anilindimethylhexylsilane and no intermediate step in its formation was noted.

Dimethylaminodimethylsilane, diethylaminodimethylsilane, and di-*n*-butylaminodimethylsilane under the same conditions formed little or no adducts with hexene-1. However these silanes added very smoothly, although slowly, to hexene-1 if *sym*-tetramethyldisilazane was in the mixture of reagents.

This strange behavior was thought to be the likely consequence of an inability of dialkylaminodimethylsilanes to form a complex with platinum necessary for catalytic activity in such a system. The formation of di-*n*-butylamino-hexyldimethylsilane then must have

(1) E. Y. Lukevits and M. G. Vorankov, "Organic Insertion Reactions of Group IV Elements," Consultants Bureau, New York, N. Y., 1966, and references cited therein.

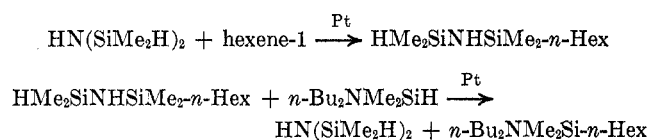
(2) K. A. Andrianov, L. M. Khanenashvili, V. M. Kopylov, and T. V. Nesteroras, *Izv. Nauk Akad. USSR, Ser. Khim.*, **2**, 351 (1968).

(3) R. O. Sauer and R. H. Hasek, *J. Amer. Chem. Soc.*, **68**, 241 (1946).

(4) S. Sujishi and S. Witz, *ibid.*, **76**, 4631 (1954).

(5) K. Hedberg, *ibid.*, **77**, 6491 (1955).

occurred by an exchange such as in the following reactions.



Di-*n*-hexyltetramethyldisilazane was mixed with octene-1 and dimethylaminodimethylsilane and the catalyst. Again, little or no reaction occurred. In the presence of 1-*n*-hexyl-1,1,3,3-tetramethyldisilazane, however, a complex mixture of products formed in excellent yields. The products included *n*-hexyldimethylaminodimethylsilane, which could result only by the exchange described above. The products also included dimethylaminodimethyloctylsilane, *sym*-dihexyltetramethyldisilazane, *sym*-dioctyltetramethyldisilazane, and 1-hexyl-3-octyltetramethyldisilazane. These products indicate that a reversible exchange of silyl groups between disilazanes and dimethylaminosilanes occurred in this system. Probably only the dimethylsilyl groups in disilazanes added to the olefins, but with the exchange going on all possible adducts were produced. In order to see if chloroplatinic acid was a catalyst for such exchange processes in the absence of an olefin, *n*-hexylmethylaminodimethylsilane and *sym*-tetramethyldisilazane were heated 20 hr at 100° with chloroplatinic acid. No exchange took place. This indicates that exchange required a platinum-olefin-silane complex. Dimethylaminosilanes are ineffective in making such a complex and are therefore not added to an olefin. Trisdimethylaminosilane was another example that did not add to hexene-1 with chloroplatinic acid nor with benzoyl peroxide.

Hexene-1, with *sym*-tetramethyldisilazane or with *sym*-diphenyldimethyldisilazane, gave the corresponding di-*n*-hexyl adducts in good yield. 3,3-Dimethoxypropene under similar conditions gave a 53% yield of *sym*-bis(3,3-dimethoxypropyl)tetramethyldisilazane. Under the same conditions pentene-2 reacted very slowly with *sym*-tetramethyldisilazane but formed a good yield of a mixture of *n*-pentyl and *sec*-pentyl adducts. This behavior of *sym*-tetramethyldisilazane with pentene-2 is closely analogous to the behavior of *sym*-tetramethyldisiloxane.⁶

sym-Tetramethyldisilazane and vinyldimethylaminodimethylsilane reacted smoothly to form *sym*-bis[2-(2-dimethylaminodimethylsilyl)ethyl]tetramethyldisilazane, (Me₂NMe₂SiCH₂CH₂SiMe₂)₂NH. This example is interesting chiefly because the large number of products were not observed that would have formed if silyl groups had exchanged extensively between the disilazane and dimethylaminosilane structures.

sym-Tetramethyldisilazane and allylamine made hydrogen and other products that were not identified. The formation of hydrogen from allylamine and silicon hydrides has been observed before.⁷

Allyl acetate, allyl chloride, methallyl chloride, methyl acrylate, and methyl methacrylate all gave numerous products which were not identified. Acrylonitrile did not seem to react with tetramethyldisilazane, but preferred to polymerize.

(6) H. M. Bank, J. C. Saam, and J. L. Speier, *J. Org. Chem.*, **29**, 792 (1964).

(7) J. C. Saam and J. L. Speier, *ibid.*, **24**, 119 (1959).

Trisdimethylsilylamine with hexene-1 formed at least five addition products detected by glc analysis. A large run was distilled to yield 41% bis(hexyldimethylsilyl)dimethylsilylamine. A mass spectrum of the products from a glc analysis indicated that the higher boiling products contained an unusual combination of hexyl and methyl groups and hydrogen on silicon. The lowest boiling peak had a *m/e* of 373 corresponding to bis(hexyldimethylsilyl)trimethylsilylamine. Three other peaks in the glc had a *m/e* of 429 suggesting trisilylamines each possessing five methyl groups, three hexyl groups, and one hydrogen, *e.g.*, bis(hexyldimethylsilyl)hexylmethylsilylamine.

These products were refluxed in ethanol for 10 days and after low boiling materials had been removed glc analysis indicated peaks with retention times of dihexylmethylethoxysilane, hexylmethylethoxysilane, and hexyldimethylethoxysilane.

Both trisdimethylsilylamine and tris(trimethylsilyl)amine were refluxed in ethanol to corroborate the method of derivatizing the above products by ethanolytic conversion to trimethylethoxysilane. Similarly trisdimethylsilylamine was converted to dimethylethoxysilane after 40 hr. These results were not to be expected in view of the reported stability of bis(methoxydimethylsilyl)trimethylsilylamine in refluxing methanol.⁸

No exchange of hydrogen and methyl groups on silicon in trisdimethylsilylamine occurred in the presence of chloroplatinic acid under the same conditions in the absence of the olefin.

The exchange of methyl groups and hydrogen from one silicon atom to another of trisdimethylsilylamine is without precedent during platinum-catalyzed addition of silicon hydrides to olefins. Methyl groups and trimethylsiloxy groups have exchanged during the addition of bistrimethylsilyloxymethylsilane to hexene-2, but in that case no exchange of hydrogen was detected.⁹

A mixture of cyclo-*N*-allylmethylsilazanes, (CH₂=CHCH₂NSiMeH)_{*n*}, was added to refluxing toluene that contained chloroplatinic acid. A very high boiling product resulted. This product was refluxed in methanol for 64 hr and distilled to obtain about a 51% yield of 2-(methylmethoxydimethylsilyl)propylamine. An isomer, thought to be 3-(methylmethoxydimethylsilyl)propylamine was also present as an impurity to the extent of about 9%.

Experimental Section

Analyses.—Gas-liquid chromatographs (glc) were obtained with an 8 ft × 0.25 in. stainless steel column packed with 26% Dow Corning SGM-11 on Chromosorb W 80-100 mesh. Peaks were identified in most cases by injection of samples to which authentic compounds had been added. ¹H nmr spectra were obtained on a Varian Associates Model A-60 using CCl₄ as solvent and tetramethylsilane as an internal standard. Infrared spectra were obtained on a Perkin-Elmer 521 grating spectrometer. The mass spectra were obtained on an AEI-MS-12 mass spectrometer. Elemental analyses were determined by the Dow Corning Analytical Laboratory. The specific refractions of the compounds in this paper were calculated with the bond refraction values of Vogel, *et al.*¹⁰

(8) L. W. Breed and R. L. Elliot, *J. Organometal. Chem.*, **11**, 447 (1968).

(9) Marilyn R. Stober, M. C. Musolf, and J. L. Speier, *J. Org. Chem.*, **30**, 1651 (1965).

(10) A. I. Vogel, W. T. Creswell, and J. Lucrester, *J. Phys. Chem.*, **58**, 174 (1954).

TABLE I
INTERMEDIATES

Compd	Registry no.	% yield	Bp, °C (mm)	n_D^{25}	d_4^{25}	R_D		Neut equiv	
						Calcd	Found	Calcd	Found
<i>n</i> -Pentyltrimethylchlorosilane	25938-34-5	88	160 (atm)	1.4225				165	169
<i>n</i> -Hexyltrimethylchlorosilane	3634-59-1	58	98-100 (50)	1.4269	0.8759	0.296	0.293	179	179
<i>n</i> -Octyltrimethylchlorosilane ^a		79	90 (30)	1.4328				209	219
<i>n</i> -Hexylmethylchlorosilane	26015-61-2	34	172 (atm)						
<i>n</i> -Hexylmethylethoxysilane	25938-35-6	43	80 (25)	1.4136	0.8091	0.313	0.309	...	^b
Di- <i>n</i> -hexylmethylsilane	1001-46-3	53	137 (20)	1.4365	0.7773	0.337	0.337	...	^c
Di- <i>n</i> -hexylmethylethoxysilane	25938-37-8	81	157 (30)	1.4320				...	^d
Dimethylaminodimethylvinylsilane ^e		42	108 (atm)	1.4169				129	133
<i>n</i> -Butylaminodimethylsilane	25938-38-9	49	88-91 (40)	1.4088	0.7591	0.318	0.318	131	135
Diethylaminodimethylsilane ^f		39	110 (atm)	1.4089					
Dimethylaminodimethylsilane ^g		28	68 (atm)	1.3889				103	105
Di- <i>n</i> -butylaminodimethylsilane	25938-39-0	39	70-71 (7)	1.4268	0.7916	0.328	0.325	187	186
<i>sym</i> -Dimethyl-diphenyldisilazane	25938-40-3	53	120-121 (0.5)	1.5480	0.9998	0.321	0.318	257	255
Anilindimethylsilane ^h			91 (12)	1.5312	0.9895	0.319	0.313	151	153
<i>sym</i> -Tetramethyldisilazane ⁱ		57	100 (atm)					133	134
Trisdimethylsilylamine ^j			150 (atm)	1.4222					
Dimethylamino- <i>n</i> -hexyldimethylsilane	25913-89-7	80	103-108 (30)	1.4278	0.9519	0.328	0.327	187	188
Diethylamino- <i>n</i> -hexyldimethylsilane	26015-62-3	75	72 (1.0)	1.4330	0.7976	0.320	0.326	215	217
<i>N</i> -Allylmethylcyclosilazanes		44.5	69-133 (0.1)	1.4791- 1.5006	0.9322- 0.9760	0.308	0.304- 0.302	99	99-100

^a R. H. Bunnell and D. A. Shirley, *J. Org. Chem.*, **17**, 1545 (1952), report bp 222-225°. ^b *Anal.* Calcd for SiC₉H₂₂O: Si, 16.1; C, 62.0; H, 12.7. Found: Si, 15.7; C, 63.1; H, 12.6. ^c *Anal.* Calcd for SiC₁₃H₃₀O: Si, 13.1; C, 72.9; H, 14.1. Found: Si, 13.2; C, 72.8; H, 14.02. ^d *Anal.* Calcd for SiC₁₅H₃₄O: Si, 10.82; C, 69.4; H, 13.2. Found: Si, 10.98; C, 69.8; H, 13.6. ^e W. J. Patterson and N. Bilow, *J. Polym. Sci., Part A-1*, **7** (4), 1089 (1969), report bp 105-106° (760 mm). ^f K. A. Andrianov, T. K. Dzhashiashvili, V. V. Astakhin, and G. N. Shunakova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **12**, 2229 (1966), report bp 112-112.5, n_D^{20} 1.8087. ^g W. J. Patterson and N. Bilow, *J. Polym. Sci., Part A-1*, **7** (4), 1089 (1969), report bp 65-66° (760 mm). ^h K. A. Andrianov, L. M. Khananashvili, V. M. Kopylou, and A. A. Vyaz'mitinova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **7**, 1539 (1969), report bp 65° (8 mm). ⁱ H. Kriegsmann and G. Engelhardt, *Z. Anorg. Chem.*, **310**, 100 (1961), report bp 99-100°. ^j R. P. Bush, N. C. Lloyd, and C. A. Pearce, *J. Chem. Soc. A*, 253 (1969), report bp 153° (760 mm).

The neutralization equivalents of the aminosilanes and disilazanes were determined by titration with 0.1 *N* perchloric acid in acetic acid to the blue methyl violet end point. The neutralization equivalents of the chlorosilanes were obtained by titration with 0.1 *N* sodium hydroxide in aqueous ethanol with phenolphthalein as an indicator.

Reagents.—Chlorosilanes were products of the Dow Corning Corporation and, with the exception of dimethylchlorosilane, were >99% pure by glc analysis. Dimethylchlorosilane was approximately 75% pure.

Allylamine was obtained from the Shell Chemical Company >95% pure by glc analysis. Ammonia and dimethylamine were obtained from Matheson Company. Di-*n*-butylamine was obtained from Aldrich Chemical Company. Diethylamine, *n*-butylamine, and aniline were obtained from Fisher Scientific Company.

Synthesis of Intermediates.—Dimethylaminosilanes and disilazanes were prepared by bubbling an excess of dimethylamine or ammonia through a stirred solution of the appropriate chlorosilane in pentane at 0°. Other aminosilanes from liquid amines were prepared by adding chlorosilanes to a solution of the amine in pentane. Trisdimethylsilylamine was prepared from tetramethyldisilazane and dimethylchlorosilane with pyridine as a hydrogen chloride acceptor. The products were warmed to room temperature and filtered. The filtrates were then distilled to obtain the products shown in Table I.

n-Pentyl-, *n*-hexyl-, and *n*-octyltrimethylchlorosilanes were prepared from pentene-1, hexene-1 or octene-1 and dimethylchlorosilane with chloroplatinic acid as the catalyst.¹¹

Di-*n*-hexylmethylsilane was prepared from *n*-hexylmagnesium bromide in ether and *n*-hexylmethylchlorosilane.

Di-*n*-hexylmethylethoxysilane was prepared by the reaction of di-*n*-hexylmethylsilane and absolute ethanol in the presence of 5% palladium on charcoal.¹² Nmr spectral data are shown in Table II.

***n*-Butylaminodimethylsilane with Hexene-1.**—*n*-Butylaminodimethylsilane, 26.0 g (0.2 mol), was added to refluxing hexene-1, 16.8 g (0.2 mol), that contained 3 drops of 0.1 *M* H₂PtCl₆. The

mixture was heated to about 100° during 1 hr and analyzed by glc. At this time it was mostly 2-*n*-butyl-1-*n*-hexyl-1,1,3,3-tetramethyldisilazane and butylamine. After 3 hr at 100° and a weekend at room temperature the product was distilled to give hexene, 7.0 g (42% of starting material), *n*-butylaminodimethylhexylsilane [17.5 g (0.086 mol, 74% based on unrecovered hexene); bp 52-54° (15 mm); n_D^{20} 1.4316; d_4^{25} 0.7893; R_D 0.328, calcd 0.327; neut equiv 214, calcd 215; ir (CCl₄) 3410 (NH), (CS₂) 1250 cm⁻¹ (SiMe)], and 2-*n*-butyl-1-*n*-hexyl-1,1,3,3-tetramethyldisilazane [6.1 g (0.022 mol, 14.7% based on unrecovered hexene); bp 69° (0.1 mm); n_D^{20} 1.4410; d_4^{25} 0.8196; R_D 0.320, calcd 0.322; ir (CCl₄) 2130 (SiH), (CS₂), 1250 (SiMe), 900 cm⁻¹ (Si-N)].

Anilindimethylhexylsilane with Hexene-1.—Hexene-1, 4.2 g (0.05 mol), anilindimethylsilane, 7.22 g (0.05 mol), and 0.01 ml of 0.1 *M* H₂PtCl₆ were sealed into a Pyrex tube and heated to 100° for 24 hr. Distillation gave 11.3 g (96%) of anilino-hexyldimethylsilane: bp 122° (1.5 mm); n_D^{20} 1.5029; d_4^{25} 0.9010; R_D 0.328, calcd 0.322; neut equiv 239, calcd 235; ir 3400 (N-H), 1500 and 1600 (Ph-N), 1253 cm⁻¹ (Si-Me).

Dimethylaminodimethylsilane with Hexene-1.—A sealed tube containing 1.03 g (10 mmol) of dimethylaminodimethylsilane and 0.84 g (10 mmol) of hexene-1 containing 0.01 ml of 0.1 *M* chloroplatinic acid was heated at 100° for 20 hr. Analysis by glc indicated less than 10% of the mixture was higher boiling than the starting materials.

Diethylaminodimethylsilane with Hexene-1.—A sealed tube containing 1.31 g (10 mmol) of diethylaminodimethylsilane, 0.84 g (10 mmol) of hexene-1 and 0.01 ml of 0.1 *M* chloroplatinic acid was heated at 100° for 18 hr. A glc analysis of this mixture indicated less than 10% eluted after the starting materials.

Di-*n*-butylaminodimethylsilane with Hexene-1.—Di-*n*-butylaminodimethylsilane, 1.87 g (10 mmol), and 0.84 g (10 mmol) hexene-1 (0.84 g, 10 mmol) with 0.01 ml of 0.1 *M* chloroplatinic acid under conditions described above gave almost no reaction.

Dimethylaminodimethylsilane with Hexene-1 and *sym*-Tetramethyldisilazane.—A sealed tube containing 1.03 g (10 mmol) of dimethylaminodimethylsilane, 0.67 g (5 mmol) of *sym*-tetramethyldisilazane, 1.68 g (20 mmol) of hexene-1, and 0.01 ml of 0.1 *M* chloroplatinic acid was heated at 100° for 20 hr. A glc of the products indicated very small amounts of hexene-1 and dimethylaminodimethylsilane, no tetramethyldisilazane,

(11) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Amer. Chem. Soc.*, **79**, 974 (1957).

(12) L. H. Sommer and J. E. Lyons, *ibid.*, **91**, 7061 (1969).

TABLE II
NMR SPECTRAL DATA

Structure	Registry no.	τ	H's	Assignment	Type	Hz
$\begin{array}{c} \text{H} \\ \\ \text{CH}_3(\text{CH}_2)_5\text{NSi}(\text{CH}_3)_2\text{H} \end{array}$	25938-38-9	9.93	6.3	SiCH ₃	s	
		9.10	3.0	CCH ₃	broad s	
		8.4-8.9	4.8	CH ₂ , NH	m	
		7.0-7.5	2.0	NCH ₂	m	
$\begin{array}{c} \text{H} \\ \\ \text{CH}_3(\text{CH}_2)_6\text{SiCH}_3(\text{OCH}_2\text{CH}_3)\text{H} \end{array}$	25938-35-6	5.55	0.9	SiH	m	
		9.87	3.0	SiCH ₃	d	4
		8.3-9.6	18.5	alkyl H	m	
		6.36	2.0	OCH ₂ CH ₃	q	7
$\begin{array}{c} \text{H} \\ \\ [\text{CH}_3(\text{CH}_2)_5]_2\text{SiCH}_3\text{H} \end{array}$	1001-46-3	5.51	1.0	SiH	q	4
		9.97	3.0	SiCH ₃	d	4
		8.3-9.7	26.0	alkyl H	m	
$\begin{array}{c} \text{H} \\ \\ [\text{CH}_3(\text{CH}_2)_5]_2\text{SiCH}_3(\text{OCH}_2\text{CH}_3) \end{array}$	25938-37-8	6.25	1.0	SiH	q	4
		≈10.0	3.0	SiCH ₃	s	
		8.7-9.7	29.0	alkyl H	m	
		6.41	2.0	OCH ₂ CH ₃	q	7
$\begin{array}{c} \\ (-\text{SiCH}_3\text{HNCH}_2\text{CH}=\text{CH}_2)_x \end{array}$		9.8-9.86	2.9	SiCH ₃	m	
		6.55	2.0	NCH ₂	m	
		4.8-5.4	3.0	SiH, C=CH ₂	m	
		4.0-4.5	1.0	-CH=CH ₂	m	
$\begin{array}{c} \text{H} \\ \\ \text{CH}_3(\text{CH}_2)_6\text{Si}(\text{CH}_3)_2\text{N}(\text{CH}_2)_3\text{CH}_3 \end{array}$	25942-76-1	10.04	6.0	SiCH ₃	s	
		9.1-9.75	21.0	alkyl H	m	
		7.32	2.0	NCH ₂	m	
$\begin{array}{c} \text{H} \\ \\ \text{CH}_3(\text{CH}_2)_6\text{Si}(\text{CH}_3)_2\text{N}[\text{Si}(\text{CH}_3)_2\text{H}][(\text{CH}_2)_3\text{CH}_3] \end{array}$	25942-77-2	9.94	6.0	SiCH ₃	s	
		9.89	6.0	SiCH ₃	d	3
		8.7-9.5	20.0	alkyl H	m	
		7.3	2.0	NCH ₂	m	
		5.58	1.0	SiH	m	3
$\begin{array}{c} \text{H} \\ \\ \text{PhNSi}(\text{CH}_3)_2(\text{CH}_2)_6\text{CH}_3 \end{array}$	25942-78-3	9.81	6.1	SiCH ₃	s	
		9.13	3.0	CCH ₃	d	
		6.84	0.9	NH	s	
		2.8-3.7	5.1	ArH	m	
$\begin{array}{c} \text{H} \\ \\ [\text{CH}_3(\text{CH}_2)_5\text{Si}(\text{CH}_3)_2]_2\text{NH} \end{array}$	25942-79-4	9.98	12.0	SiCH ₃	s	
		8.5-9.7	27.0	alkyl H, NH	m	
$\begin{array}{c} \text{H} \\ \\ \text{CH}_3(\text{CH}_2)_5\text{Si}(\text{CH}_3)_2\text{NSi}(\text{CH}_3)_2\text{H} \end{array}$	25938-25-4	9.98	6.0	SiCH ₃	s	
		9.89	6.0	SiCH ₃	d	3
		9.12-9.7	14.0	alkyl H, NH	m	
		5.55	1.0	SiH	m	3
$\begin{array}{c} \text{H} \\ \\ \text{CH}_3(\text{CH}_2)_6\text{Si}(\text{CH}_3)_2\text{NSi}(\text{CH}_3)_2(\text{CH}_2)_7\text{CH}_3 \end{array}$	25938-26-5	10.0	12.0	SiCH ₃	s	
		8.7-9.7	31.0	alkyl H, NH	m	
$\begin{array}{c} \text{H} \\ \\ \text{CH}_3(\text{CH}_2)_4\text{Si}(\text{CH}_3)_2\text{NSi}(\text{CH}_3)_2\text{H} \end{array}$	25938-27-6	≈9.9	12.0	SiCH ₃	m	
		8.5-8.8	12.0	alkyl CH ₂	m	
		5.67	1.0	SiH	m	
$\begin{array}{c} \text{H} \\ \\ (\text{CH}_3)_2\text{SiN}[\text{Si}(\text{CH}_3)_2(\text{CH}_2)_6\text{CH}_3]_2 \end{array}$	25938-28-7	9.8	21.0	SiCH ₃	m	
		8.4-9.6	16.0	alkyl H	m	

and large amounts of *sym*-dihexyltetramethyldisilazane and dimethylaminohexyldimethylsilane.

Diethylaminodimethylsilane with Hexene-1 and *sym*-Tetramethyldisilazane.—Hexene-1, 50.4 g (0.6 mol), was slowly added to a solution of 19.6 g (0.15 mol) of diethylaminodimethylsilane and 26.6 g (0.20 mol) of *sym*-tetramethyldisilazane with 0.1 ml of 0.1 M chloroplatinic acid was refluxed overnight. The products were distilled through a Vigreux column. All fractions containing dimethylamino-*n*-hexyldimethylsilane were combined and redistilled through a spinning-band column to give 15.2 g,

40% of product: bp 75° (2 mm); n_D^{25} 1.4338; neut equiv 217, calcd 215.

Di-*n*-butylaminodimethylsilane, Hexene-1, and *sym*-Tetramethyldisilazane.—Hexene-1, 25.8 g (0.3 mol), was added slowly to di-*n*-butylaminodimethylsilane, 28.4 g (0.15 mol), and *sym*-tetramethyldisilazane, 10 g (0.075 mol), that contained 0.1 ml of 0.1 M H₂PtCl₆. The solution was refluxed 72 hr before analysis by glc indicated that the reagents had nearly completely reacted. Distillation did not separate di-*n*-butylaminodimethylsilane and *sym*-dihexyltetramethyldisilazane although they

were distinguishable by glc analysis. One fraction contained 76 area per cent of the former, 23 area per cent of the latter and had a neut equiv of 281. Calcd (for such a mixture) 280.

sym-Dihexyltetramethylsilazane and sym-Tetramethylsilazane.—A sealed tube containing 1.87 g (10 mmol) of dimethylaminohexyldimethylsilane and 1.33 g (10 mmol) of *sym*-tetramethylsilazane containing 0.01 ml of 0.1 *M* chloroplatinic acid was heated at 100° for 20 hr. A glc analysis indicated only starting materials.

Dimethylaminodimethylsilane with Octene-1 in the Presence of sym-Dihexyltetramethylsilazane.—A sealed tube containing 1.5 g (5 mmol) of *sym*-di-1,1,3,3-tetramethylsilazane, 0.5 g (5 mmol) of dimethylaminodimethylsilane and 0.56 g (5 mmol) of octene-1 was heated for 72 hr at 110°. A glc analysis of the product mixture indicated no dimethylaminohexyldimethylsilane and the starting materials accounted for greater than 90% of the material present.

Dimethylaminodimethylsilane and 1-n-Hexyl-1,1,3,3-tetramethylsilazane with Octene-1.—A sealed tube containing 0.87 g (4 mmol) of 1-n-hexyl-1,1,3,3-tetramethylsilazane, 0.41 g (4 mmol) of dimethylaminodimethylsilane, and 0.45 g (4 mmol) of octene-1 was heated at 120° for 24 hr. A glc analysis of the mixture indicated the following compounds had formed: dimethylaminohexyldimethylsilane, 1-n-hexyl-1,1,3,3-tetramethylsilazane, dimethylaminodimethyloctylsilane, *sym*-di-*n*-hexyltetramethylsilazane, 1-n-hexyl-1,1,3,3-tetramethyloctylsilazane, and a higher boiling material which probably was *sym*-tetramethyloctylsilazane, although no standard was available to identify it.

Trisdimethylaminosilane with Hexene-1 with Chloroplatinic Acid.—A sealed tube containing 1.6 g (10 mmol) of trisdimethylaminosilane and 0.84 g (10 mmol) of hexene-1 containing 0.01 ml of 0.1 *M* chloroplatinic acid was heated at 100° for 20 hr. A glc analysis indicated no reaction had taken place.

Trisdimethylaminosilane with Hexene-1 with Benzoyl Peroxide.—Benzoyl peroxide (50 mg) was added to a refluxing solution of 8.3 g (0.096 mol) of hexene-1 and 16.1 g (0.1 mol) of trisdimethylaminosilane. After 4 hr another 10 mg of benzoyl peroxide was added. After 22 hr 25 mg was added, and after 48 hr analysis by glc indicated no reaction had taken place.

sym-Di-*n*-hexyldimethyldiphenylsilazane with Hexene-1.—A sealed tube containing 2.6 g (10 mmol) of *sym*-diphenyldimethylsilazane and 1.68 g (20 mmol) of hexene-1 with chloroplatinic acid was heated at 100° for 20 hr. Analysis by glc indicated one high boiling compound: n_{25}^D 1.5188; d_{25}^{25} 0.9477; R_D 0.320, calcd 0.322; neut equiv 417, calcd 426.

Bis[2-(dimethylaminodimethylsilyl)ethyl dimethylsilyl]amine, (Me₂NMe₂SiCH₂CH₂SiMe₂)₂NH.—To 25.8 g (0.2 mol) of refluxing vinyl dimethylaminodimethylsilane containing 0.3 ml of 0.1 *M* chloroplatinic acid was added slowly, 13.3 g (0.1 mol) of *sym*-tetramethylsilazane. Distillation of the product gave 20.5 g, 53%; bp 120–125° (2 mm); n_{25}^D 1.4578; d_{25}^{25} 0.8752; R_D 0.312, calcd 0.314; neut equiv 134.3, calcd 130.3.

2-(Methyldimethoxysilyl)propylamine.—To a refluxing solution of 0.1 ml of 0.1 *M* chloroplatinic acid in 50 ml of toluene was slowly added 50 g (0.5 mol) of *N*-allylmethylcyclosilazane. The mixture was refluxed for 20 hr and cooled to 70°, and 50 ml of methanol was added. The mixture was then refluxed for 64 hr. A glc analysis revealed a small amount of methyltrimethoxysilane and a large amount of two products thought to be isomers, methyldimethoxysilylpropylamines with one isomer predominating in a ratio of >9:1. The major isomer was isolated by distillation in 51% yield and identified as 2-(methyldimethoxysilyl)propylamine: bp 123–124° (130 mm); n_{25}^D 1.4258; d_{25}^{25} 0.9532; R_D 0.269, calcd 0.272; neut equiv 169, calcd 163; nmr τ 9.04 (d, CHCH₃, *J* = 1.5 Hz); ir 1384 cm⁻¹ (C–CH₃).¹³

sym-Tetramethylsilazane with Hexene-1.—*sym*-Tetramethylsilazane, 13.3 g (0.1 mol), was added to refluxing hexene-1, 16.8 g (0.2 mol), that contained 0.03 ml of 0.1 *M* H₂PtCl₆. After 2 hr at 67–140° glc revealed only one product. Distillation gave 26.1 g (87%): bp 100° (0.8 mm); n_{25}^D 1.4419; d_{25}^{25} 0.8149; R_D 0.3244, calcd 0.3245; neut equiv 308, calcd 302; ir (CCl₄) 3375 NH (CS₂), 1245 (SiMe), 1180 (SiNHSi), 930 (SiN), 835 cm⁻¹ (SiMe₂). *Anal.* Calcd for Si₂C₁₆H₃₀N: Si, 63.7; H, 13.1; N, 4.65. Found: Si, 63.7; H, 13.2; N, 4.64.

(13) A. D. Petrov, L. K. Freidlin, G. I. Kudryautsev, T. A. Sladkova, V. M. Vdovin, and T. I. Shein, *Chem. Zentralbl.*, 2947 (1961), report for 3-(methyldimethoxysilyl)propylamine bp 58–60° (4 mm), d_{25}^{25} 0.9430, n_{25}^D 1.4325.

1-Hexyl-1,1,3,3-tetramethylsilazane.—In the same manner *sym*-tetramethylsilazane, 34 g (0.25 mol), was heated with hexene-1, 21 g (0.25 mol). Distillation gave 24.3 g, 44.7%, of 1-n-hexyl-1,1,3,3-tetramethylsilazane: bp 90° (6 mm); n_{25}^D 1.4280; d_{25}^{25} 0.8035; R_D 0.320, calcd 0.323; ir (CCl₄) 3385 (NH), 2115 (SiH) (CS₂), 1170 cm⁻¹ (SiNSi).

sym-Bis(3,3-dimethoxypropyl)tetramethylsilazane.—To 20.4 g (0.2 mol) of 3,3-dimethoxypropene containing 3 drops of 0.1 *M* chloroplatinic acid was slowly added with heating 13.4 g (0.1 mol) of *sym*-tetramethylsilazane. The mixture was heated to 150° and then allowed to cool. A glc of the crude mixture indicated 78% of the diadduct and a mixture of at least six different lower boiling compounds. Distillation of a portion of this material gave *sym*-bis(3,3-dimethoxypropyl)tetramethylsilazane: bp 121° (0.25 mm); n_{25}^D 1.4452; d_{25}^{25} 0.9501; R_D 0.280, calcd 0.282; ir (CCl₄) 3370 (NH), 2830 (COCH₃) (CS₂), 1253 (SiCH₃), 1175 (SiNSi), 1120 (COC), 930 cm⁻¹ (SiN). *Anal.* Calcd for Si₂C₁₄H₃₀NO₂: Si, 16.7; C, 49.9; H, 10.5; N, 16.7. Found: Si, 16.8; C, 50.0; H, 10.5; N, 16.8. Treatment of this compound with acidic 2,4-dinitrophenylhydrazine solution gave the dihydrazone of tetramethylsiloxane-1,3-dipropanal, mp 184–185°, mixture melting point undepressed.

1-Hexyl-1,1,3,3-tetramethylsilazane with Octene-1.—To a refluxing solution of 0.03 ml of chloroplatinic acid in 11 g (0.1 mol) of octene-1 was slowly added 11 g (0.05 mol) of 1-hexyl-1,1,3,3-tetramethylsilazane. The reaction was complete in 1 hr and distillation gave 13.7 g (83%) of 1-hexyl-1,1,3,3-tetramethyl-3-octylsilazane: bp 138° (0.8 mm); n_{25}^D 1.4439; d_{25}^{25} 0.8240; R_D 0.323, calcd 0.325.

sym-Tetramethylsilazane with Pentene-2 at 100° for 40 Hr.—A sealed tube containing 14.0 g (0.2 mol) of pentene-2 and 13.3 g (0.1 mol) of *sym*-tetramethylsilazane with 0.1 ml of 0.1 *M* chloroplatinic acid solution was heated at 100° for 40 hr. Analysis by glc revealed that all of the starting disilazane had reacted, however, approximately one-half of the olefin was still present. The monoadduct was distilled to give 12.8 g (63%): bp 138–140° (140 mm); n_{25}^D 1.4340; d_{25}^{25} 0.8084; R_D 0.320, calcd 0.324; neut equiv 208, calcd 203; ir (CCl₄) 3380 (NH), 2115 (SiH) (CS₂), 1170 (SiNHSi), 840 cm⁻¹ (SiMe₂). *Anal.* Calcd for Si₂C₉H₂₀N: Si-H, 0.49. Found: Si-H 0.535.

sym-Tetramethylsilazane with Pentene-2 at 110° for 48 Hr.—Four sealed tubes containing 14.0 g (0.2 mol) of pentene-2 and 13.3 g (0.1 mol) of 1 with 0.03 ml of 0.1 *M* chloroplatinic acid were heated at 110° for 48 hr. The contents of the sealed tubes were combined and distilled to give 55.5 g (68%) of monopentyladduct, bp 57° (2 mm), and 17 g (15.6%) of dipentyladduct: bp 84–86° (1 mm); n_{25}^D 1.4118; d_{25}^{25} 0.7570; R_D 0.324, calcd 0.329. This product 51 g (0.25 mol) in 50 ml of pentane was converted into chlorosilanes by a slow stream of dry hydrogen chloride during 6.5 hr. The solution was filtered and distilled. A fraction, bp 33–36°, was a mixture of pentane and dimethyl-dichlorosilane. No trimethylchlorosilane was detected by glc analyses. A fraction of pentyldimethylchlorosilane, 18.7 g (46%), bp 62–63° (20 mm), contained two peaks by glc analysis with similar retention times, one of them being *n*-pentyldimethylchlorosilane: ir (CCl₄) 1376 (C–CH₃) (CS₂), 1250 (SiMe), 510 cm⁻¹ (SiCl); nmr τ 8.3–9.3 (11, alkyl CH) 9.63, 9.66 (6, SiCH₃). The C–CH₃ absorption in the infrared was greater than in the spectrum of *n*-pentyldimethylchlorosilane and two absorptions in the SiCH₃ region of the nmr spectrum indicate *sec*-pentyl derivatives.

sym-Tetramethylsilazane and Allylamine.—A sealed tube containing 1.14 g (20 mmol) of allylamine, 1.33 g (10 mmol) of *sym*-tetramethylsilazane, and 0.01 ml of 0.1 *M* chloroplatinic acid was heated at 100° for 20 hr. The tube at –80° exploded violently when it was opened.

sym-Tetramethylsilazane and Acrylonitrile.—A sealed tube containing 1.06 g (20 mmol) of acrylonitrile, 1.33 g (10 mmol) of *sym*-tetramethylsilazane, and 1 drop of 0.1 *M* chloroplatinic acid was heated at 100° for 20 hr. There was no evidence of addition by glc analysis. A similar experiment at 150° for 64 hr formed a large amount of solid polyacrylonitrile.

sym-Tetramethylsilazane with Other Compounds.—*sym*-Tetramethylsilazane was heated in sealed Pyrex tubes with H₂PtCl₆ and methyl methacrylate, methyl acrylate, allyl chloride, methallyl chloride, and allyl acetate. In each case the reagents were consumed to make a large number of products. These mixtures were not examined further.

Trisdimethylsilylamine with Hexene-1.—Five sealed tubes containing a total of 57.0 g (0.3 mol) of trisdimethylsilylamine

and 100.1 g (1.2 mol) of hexene-1 were heated at 115° for 72 hr. Each tube contained 0.03 ml of 0.1 *M* chloroplatinic acid. A glc analysis of the crude product revealed one major and four minor components. Distillation of 83 g of this material gave 23.3 g (41%) of bis(*n*-hexyldimethylsilyl)dimethylsilylamine: bp 110° (1 mm); n_D^{25} 1.4569; neut equiv 368, calcd 359; ir (CCl₄) 2130 (SiH) (CS₂), 900–920 cm⁻¹ (SiN); nmr τ 9.87 (s, 12, SiCH₃), 9.74 (d, 6, HSiCH₃), 8.4–9.6 (26, alkyl-H) 5.44 (m, 0.8, SiH). One of the minor components was isolated from a separate experiment with trisdimethylsilylamine and hexene-1 and identified as bis(*n*-hexyldimethylsilyl)trimethylsilylamine: bp 115° (1 mm); n_D^{25} 1.4611; neut equiv 373, calcd 373; ir (CS₂) 1250–1260 (multiplet SiMe), 840 (SiMe₃), 910 cm⁻¹ (SiN).

The residue from the distillation of the above 83 g of material was analyzed by a combination of glc and mass spectra. Three peaks in the glc had a *m/e* ratio of 429 for a molecular ion corresponding to Si₃C₂₃H₆₅N. This corresponds to Hex₃Me₃HSi₃N.

A solution of 17 g of this residue in 50 ml of ethanol with \approx 100 mg of ammonium chloride was refluxed for 10 days. The volatiles were removed *in vacuo* and a glc of the resulting products had a large peak corresponding to hexyldimethylethoxysilane and smaller peaks for hexylmethylethoxysilane and dihexylmethylethoxysilane as indicated by coinjection with authentic samples.

Registry No.—Bis-[2-(dimethylaminodimethylsilyl)-ethyldimethylsilyl]amine, 25938-29-8; 2-(methyldimethoxyethyl)propylamine, 25938-30-1; *sym*-bis(3,3-dimethoxypropyl)tetramethyldisilazane, 26344-26-3; bis-(*n*-hexyldimethylsilyl)dimethylsilylamine, 25938-32-3; bis-(*n*-hexyldimethylsilyl)trimethylsilylamine, 25938-28-7.

A Novel Reaction of Saturated Aliphatic Acids with Aromatic Compounds in the Presence of Palladium(II) Chloride. The Formation of Cinnamic Acid Derivatives

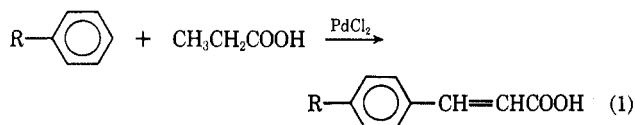
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Saturated aliphatic acids with α and β hydrogens, such as propionic, *n*- and isobutyric acid, reacted with aromatic compounds and palladium(II) salts in the presence of alkali metal carboxylates to give cinnamic acid derivatives. The addition of some solvents, such as an acid anhydride, tetrachloroethylene, or acetonitrile, resulted in significant differences in products formed. A mechanism involving the formation of an intramolecular π complex of palladium acrylate (D) has been suggested for the dehydrogenation step.

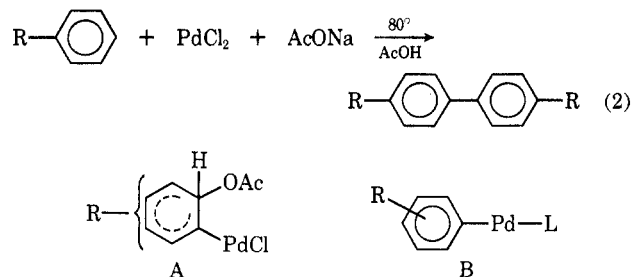
In a previous communication,¹ we reported on the novel carboxyvinylation of aromatic compounds by saturated aliphatic acids and palladium(II) chloride to give cinnamic acid derivatives.



As is well known, aromatic α,β -unsaturated acids can be synthesized by the reaction of aromatic aldehydes, ketones, or olefins with appropriate agents.² Also, with palladium(II) chloride, various cinnamates are successfully obtained from the reactions of unsaturated esters with benzenes.³ However, our work is unique in

that cinnamic acids are formed in one step from aromatic compounds and saturated aliphatic acids. This reaction is very interesting, since the formation of α,β -unsaturated aliphatic acids *via* dehydrogenation of saturated aliphatic acids by metal salts is unknown.

The reaction of aromatic compounds with palladium(II) chloride has been reported by van Helden and Verberg⁴ to give biphenyl derivatives. They proposed that the reaction proceeds *via* dimerization of a π -cyclohexadienyl complex (A). Davidson and Triggs⁵ suggested the presence of unstable phenylpalladium(II) complex (B) by analogy with the reaction of aromatic compounds with other metal acetates. Furthermore,

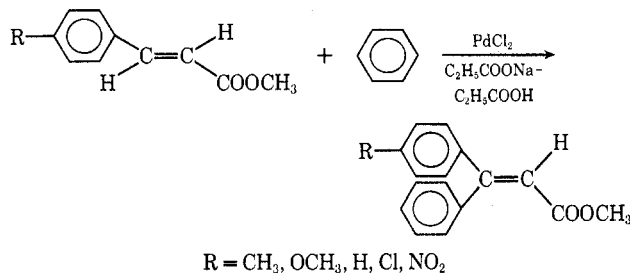


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(2) (a) W. Perkin, *J. Chem. Soc.*, **21**, 53, 181 (1868); **31**, 388 (1877). (b) J. Johnson, *Org. React.*, **1**, 210 (1942). (c) E. Knoevenagel, *Chem. Ber.*, **31**, 2596 (1898); O. Doebner, *ibid.*, **33**, 2140 (1900). (d) S. Reformatsky, *ibid.*, **20**, 1210 (1887); R. Shriner, *Org. React.*, **1**, 1 (1942). (e) M. Kharasch, S. Kane, and H. Brown, *J. Amer. Chem. Soc.*, **64**, 333 (1942).

(3) Unpublished work. Various aromatic α,β -unsaturated esters were phenylated by palladium(II) chloride to give β -phenylcinnamates in 40–50% yields.



it was reported that some olefins reacted with aromatic compounds in the presence of palladium(II) acetate to give phenylated olefins.⁶ That these reactions proceed *via* a similar phenylpalladium(II) complex (B) is supported by the reaction of *N,N*-dimethylbenzylamine-palladium complex with styrene to form a stilbene deriv-

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