

Unexpected Silicon Group Transfer in Difunctional Alkoxy Silanes

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Abstract:

During the hydrosilylation reaction of a difunctional silane with allyl glycidyl ether (AGE), two scrambled hydrosilylation products were produced in significant amounts. This scrambling is reaction condition dependent and has been observed in a few other examples. It appears to be the first such alkoxy silane transformation to occur under these conditions, although similar siloxane transformations have been documented. This also introduces a method of preparing certain organofunctional alkyldialkoxysilanes in high purities via hydrosilylation, where the close boiling rearrangement by-products are minimized.

Introduction

Organofunctional alkoxy silanes have been established as coupling agents, adhesion promoters, or cross-linking agents in applications involving glass fibers, inorganic fillers, organic polymers, filled thermoplastics, a variety of coatings, and high-performance sealants. As far as extent of application, most of such organofunctional silanes in commercial use have been trialkoxysilanes, those having three reactive alkoxy groups attached to each silicon atom, in addition to one organofunctional group. Their process chemistries take place in relatively high yields, and provide products in relatively high purities, following product isolation. The related alkyldialkoxysilanes have not achieved the same level of commercial success. Reasons include difficult preparation, as well as the fact that hydrosilylation reactions of difunctional hydrosilanes are generally more susceptible to undesired side reactions than the corresponding trifunctional analogues. These differences are reflected in less efficient processes, lower yields, and higher prices for organofunctional alkyldialkoxysilanes, making them less accessible in the marketplace.

There is increasing commercial need, however, for organofunctional alkyldialkoxysilanes in terms of product performances. In a variety of applications, certain organofunctional alkyldialkoxysilanes provide performance advantages relating to intermediate and final product properties, such as higher elongation, lower modulus, and slower cure rate. The latter is of significance in that slower cure rates allow for applications in aqueous or waterborne systems.¹ Addressing this increasing commercial need has led to the

definition of an additional undesired side reaction, namely an alkyl/alkoxy group exchange, which can prevent the attainment of desired high product purities through formation of close-boiling by-products. The following discussion presents processes by which this unexpected exchange can be minimized, if not eliminated.

There are many known examples of hydrosilylation reactions between hydroalkyldialkoxysilanes, namely methyldimethoxysilane or methyldiethoxysilane, and a wide variety of olefins.² While numerous hydrosilylation reactions have been run by adding the olefinic reactant to the hydrosilane or hydrosiloxane reactant, that mode of combination has been used to minimize side reactions other than alkyl/alkoxy group exchange.³ When methyldiethoxysilane is treated with chloroplatinic acid under hydrosilylation conditions, a hydrogen/alkoxy exchange reaction is reported, without alkyl/alkoxy exchange.⁴ There appears to be no known example of alkyl/alkoxy group exchange reaction occurring during hydrosilylation reactions of hydroalkyldialkoxysilanes with olefins. The closest related chemistry appears to be a methyl/trimethylsiloxy group exchange which occurs when internal olefins (2-hexene, cyclohexene) are hydrosilylated with bis(trimethylsiloxy)methylsilane, (Me₃SiO)₂MeSiH.⁵ Alkyl/alkoxy group exchange reactions have been reported for simple methylalkoxysilanes at high temperatures with strong base catalysts, but these involve neither hydroalkyldialkoxysilanes nor hydrosilylatable olefins.^{6a} There is some similarity to the chloroplatinic acid-catalyzed methyl/chlorine exchange observed by Benkeser and Beck,^{6b} West et al.,^{6c} and Hengge^{6d} for methylsilanes or methylated polysilanes in the presence of trichlorosilane, but the absence of olefin.

- (2) Plueddemann and Fanger report the respective reactions of dimethylethoxysilane, methyldiethoxysilane, and triethoxysilane with allyl glycidyl ether as giving single products in substantially quantitative yields without presenting purity data, while isomeric products were detected in a related hydrosilylation of butadiene monoepoxide. In each case, the hydrosilyl reactant was added to the olefinic epoxide. Plueddemann, E. P.; Fanger, G. *J. Am. Chem. Soc.* **1959**, *81*, 2632. In the same journal, Goodman et al., report the hydrosilylations of vinyl ethyl ether, vinyl *n*-butyl ether, and allylidene diacetate with methyldiethoxysilane by adding the olefin to the silane. Goodman, L.; Silverstein, R. M.; Benitez, A. *J. Am. Chem. Soc.* **1957**, *79*, 3073.
- (3) Schilling, C. L., Jr. U.S. Patent 4,160,775, 1979 and Bowman, M. P.; Schilling, C. L., Jr. U.S. Patent 5,559,264, 1996.
- (4) *Chem. Abstr.* **1975**, *82*, 16884v; Belyakova, Z. V.; Belikova, Z. V.; Yamova, M. S. *Zh. Obshch. Khim.* **1974**, *44*, 1778 (in English as *J. Gen. Chem., USSR* **1974**, *44*, 1744).
- (5) Stober, M. R.; Musolf, M. C.; Speier, J. L. *J. Org. Chem.* **1965**, *30*, 1651.
- (6) (a) Ryan, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 4730. (b) Beck, K. R.; Benkeser, R. A. *J. Organomet. Chem.* **1970**, *23*, 35; Beck, K. R. *Diss. Abstr.* **1970**, *31B*, 1813. (c) West, R. *Abstracts*; 12th Organosilicon Symposium, 1978; p 8. (d) Hengge, E.; Peter, W. *J. Organomet. Chem.* **1978**, *148*, C22.

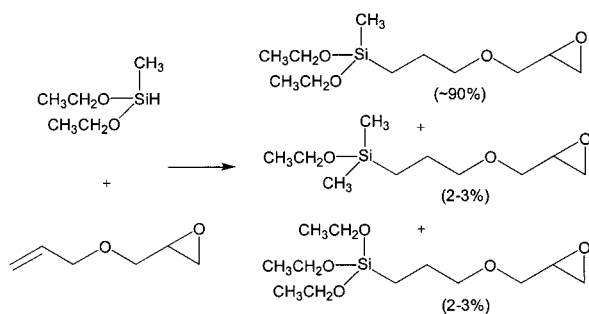
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[†] Process R&D.

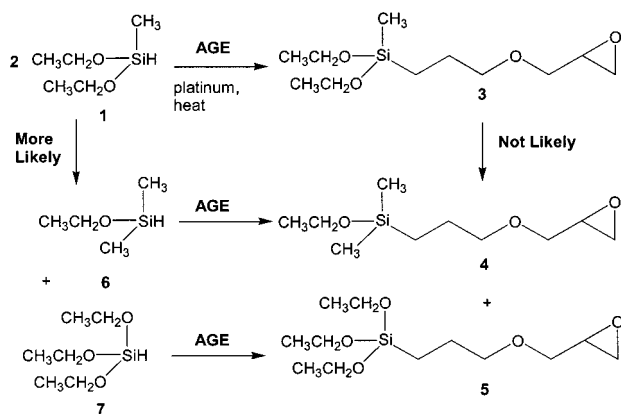
[‡] Applications R&D.

(1) Huang, M. W. U.S. Patent 6,001,907, 1999.

Scheme 1



Scheme 2



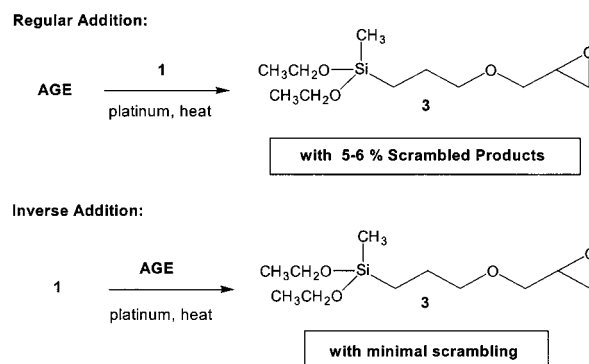
Results and Discussion

Inverse addition of allyl glycidyl ether to methyl-diethoxy-silane (**1**) in the presence of chloroplatinic acid catalyst (CPA) and acetic acid had given a small yield advantage over regular silane addition to the allyl glycidyl ether (AGE) olefin (**2**). Plans for this mode of hydrosilylation addition were mediated by concerns involved with heating a kettle of hydrosilane and led to initially running the regular addition reaction. On a larger scale, production purities were lower than anticipated primarily due to the appearance of two unknown compounds (**4**, **5**) during the hydrosilylation. These two materials had boiling points very close to that of the normal hydrosilylation product, glycidyl-oxypropylmethyl-diethoxy-silane (**3**) and comprised about 5–6% of the total material. Subsequent GC–MS analysis supported the identities of the two unknowns as dimethylethoxysilyl- and triethoxysilyl- analogues of the desired product in Schemes 1 and 2.

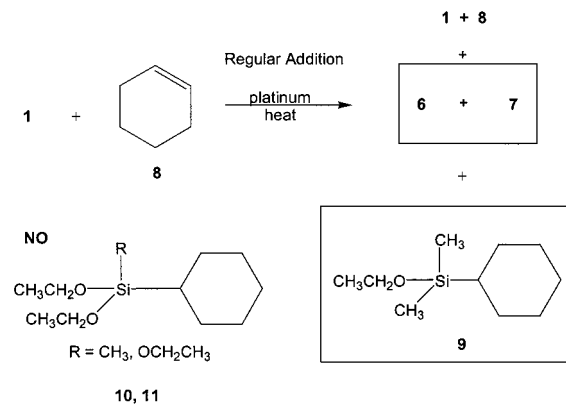
What appeared to have occurred was a silyl group transfer between two methyl-diethoxy moieties, most likely as the hydrosilane starting material. This is supported by the fact that the scrambled compounds appeared before the end of the reaction and did not increase during subsequent heating of the crude reaction product (Scheme 3). In addition, analytical evidence from many later reactions suggests that the alkyl/alkoxy group exchange reaction occurs at the reactant stage, that is, with the hydroalkyldialkoxysilane.

To eliminate other possible sources of the scrambled silanes, a fresh sample of methyl-diethoxy-silane was examined by GC–MS for scrambled material. The 97.8% purity material also contained 0.8% methyltriethoxy-silane, 0.2% ethanol, and 1.2% of related siloxanes, but no dimethyl-

Scheme 3



Scheme 4



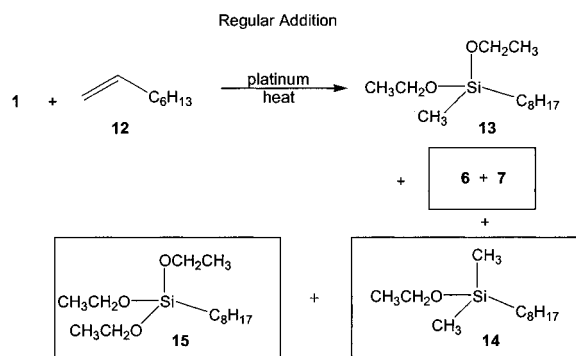
ethoxysilane or triethoxysilane. In addition, a sample of the methyl-diethoxy-silane heated to 80 °C for several hours in the presence of chloroplatinic acid and acetic acid for stability study purposes also underwent GC–MS analysis. The results were basically the same as those of Belyakova et al. in ref 4, where the major constituents besides the alkyl-dialkoxysilane, were methyltriethoxy-silane and related disiloxanes of both the starting silane and methyltriethoxy-silane.

It is of interest to note that while the exchanged precursors are probably formed in equimolar amounts their hydrosilylation reactivities are different. $R_2(RO)SiH$ appears to react more rapidly than $(RO)_3SiH$, causing an imbalance of exchanged hydrosilylation products if there is a deficiency of olefinic reactant. It is possible that the alkyl/alkoxy exchange reaction occurs to a greater extent late in hydrosilylation reactions, when much of the olefinic reactant is present in isomerized, less-reactive form. It is this situation, among others, which is avoided by running hydrosilylations by adding the olefinic reactant to the hydroalkyldialkoxysilane reactant. The AGE hydrosilylation is shown, with the exchanged precursors also undergoing hydrosilylation reactions with the olefin. AGE is well-known for isomerizing in the presence of metal catalysts to its less reactive propenyl isomers.⁷

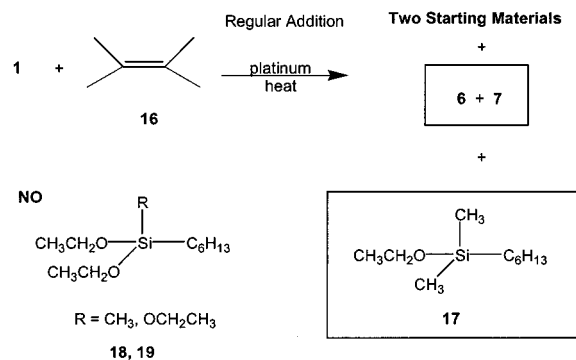
The reaction with cyclohexene (**8**) (Scheme 4) gave only starting materials with a small amount of dimethylethoxysilane (**6**) and triethoxy-silane (**7**), thus supporting the mechanism of silyl group transfer in the hydrosilane reactant. Also

(7) See, for example: Crivello, J. V.; Kim, W.-G. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, 32, 1639.

Scheme 5



Scheme 6



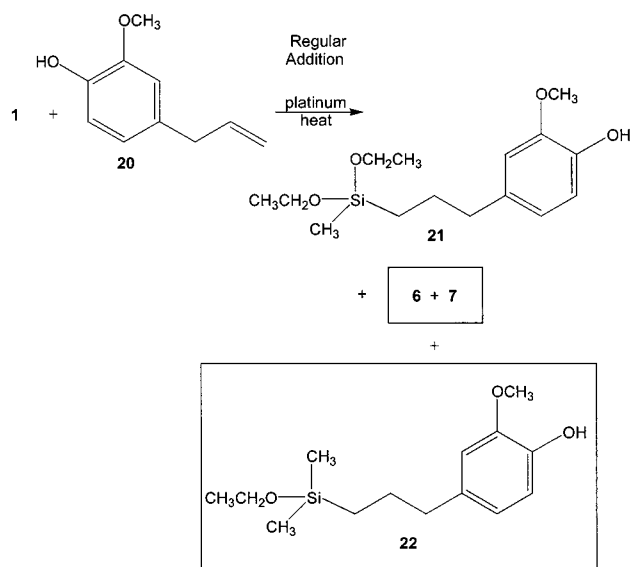
present were trace amounts of the dimethylethoxycyclohexane product (**9**). Apparently, this was the only silane in the reaction mixture able to react with the internal double bond.

The reaction of less hindered 1-octene (**12**) with difunctional silane **1** gave the normal hydrosilylation product, methyl-diethoxysilyloctane (**13**), along with the two scrambled reactants (**6,7**) as well as products (**14,15**) (Scheme 5). Both starting materials were also present. 1-Octene tends to isomerize in reaction mixtures to the less reactive 2-octene. In fact, the olefins are in equilibrium in the reaction mixture. With proportionally more of the internal alkene present as the normal hydrosilylation progresses, the environment is conducive for the silyl transfer to take place.

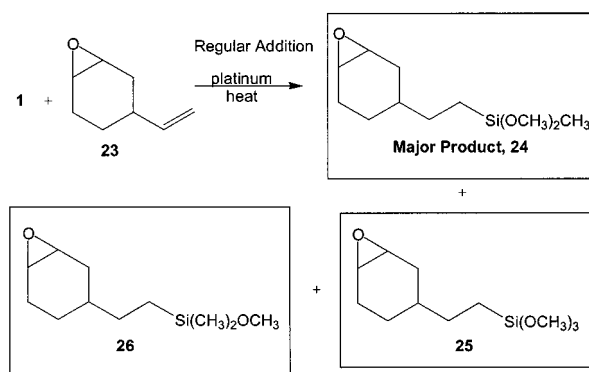
The severely hindered 2,3-dimethyl-2-butene (**16**) was investigated using the same conditions of regular addition of the olefin to a heated mixture of methyl-diethoxysilane, CPA, and acetic acid (Scheme 6). It was not really anticipated to have any hydrosilylation products because of the hindered tetrasubstituted olefin involved. Inspection of the reaction mixture after several hours showed mostly starting materials. However, small amounts of the two aforementioned scrambled hydrosilanes (**6,7**) were present. In addition, a trace amount of a 2,3-dimethyl-2-butene adduct (**17**) was observed by GC-MS.

The next example, eugenol (**20**), also gave similar results (Scheme 7). Although this is also a terminal olefin, eugenol has a tendency to isomerize to its propenyl isomer in the presence of CPA and heat. The reaction with methyl-diethoxysilane gave residual reactants, isomerized eugenol, and the normal hydrosilylation product (**21**) in addition to the two silyl scrambled hydrosilanes. Also present was the sole scrambled product derived from eugenol (**22**). Since eugenol

Scheme 7



Scheme 8



appears to be relatively free of steric hindrance toward hydrosilylation, the isoeugenol which forms likely has a retarding effect.

Last, a different example of olefin shows the same scrambling when reacted with methyl-diethoxysilane (Scheme 8). Vinylcyclohexene oxide (**23**), while giving 82–84% of expected product (**24**), also showed small percentages of the products of silyl group transfer (**25, 26**).

Conclusions

In summary, we have reported an unexpected and unprecedented silyl group transfer between alkylalkoxysilanes. This is the first known example of alkyl/alkoxy scrambling between silane compounds. The amount of scrambled product formed is small compared to either desired product or unreacted starting material, but can impact the desired product yield. Again, it appears that mode of addition controls the amount of scrambling that occurs. While regular addition of the difunctional methyl-diethoxysilane to an olefin creates an opportunity for silyl substituent scrambling, the opposite addition mode of olefin to silane nearly suppresses this side reaction. Inverse hydrosilylation appears to be the preferred mode of reaction to ensure the highest yield of hydrosilylation products, such as γ -glycidoxypropylmethyl-diethoxysilane (**3**).⁸

The scrambling most likely occurs between the Si–H reactants as an alternative reaction pathway competing with a slow hydrosilylation reaction. This is evidenced by appearance of scrambled hydrosilanes in the attempted reaction of methyldiethoxysilane with hindered olefins. It is worth noting that the related methyldimethoxysilane undergoes the same unexpected scrambling in similar reactions using the regular hydrosilylation addition of silane to olefin.

Experimental Section

Reaction pressures are normally atmospheric. Purification, as by distillation, is typically run under vacuum. The processes can be practiced in a variety of equipment ranging from small laboratory glassware through pilot scale to large production units. The abbreviations g, mL, mm, mol, ppm, μL , L, lb, kg, GC, and MS respectively represent gram, milliliter, millimeter, molar equivalent, parts per million, microliter, liter, pound, kilogram, gas chromatography, and mass spectrometry. All temperatures are reported in degrees Celsius, and all reactions were run in standard laboratory glassware or pilot scale or production units at atmospheric pressure under an inert atmosphere of nitrogen, and all parts and percentages are by weight. Reagents were used without further purification.

All reactions were monitored by gas chromatography. The instrument used was a Hewlett-Packard 6890 Series GC. Product purities also determined by analysis on this GC. Compound identification was determined by GC–MS analysis. The GC–MS instrument used was a Varian Saturn 2000 GC/MS/MS in conjunction with a Varian 3800 gas chromatograph.

Hydrosilylation of Methyldiethoxysilane (1) and Allyl Glycidyl Ether (2) (Scheme 1). To a 250 mL four-neck round-bottom flask, equipped with stir bar, thermocouple probe, condenser, addition funnel, and nitrogen inlet/outlet, was added 70.8 g (0.62 mol) of allyl glycidyl ether (AGE). A 20% excess of the raw material was used in the preparation, as some isomerization of AGE occurs in the presence of heat and platinum catalyst. A solution of 10% chloroplatinic acid in ethanol (CPA, 78 μL , 15 ppm Pt) catalyst and 90 μL (650 ppm) of acetic acid promoter are added to the AGE in the reaction vessel. The mixture was then heated to 85 °C. Methyldiethoxysilane (67.0 g, 0.52 mol), which had been charged to the addition funnel, was then added dropwise to the heated mixture at such a rate as to keep the pot temperature between 85 and 90 °C. After silane addition completion (about 80 min), the reaction was then heated at 85 °C for 30 min. GC Analysis showed, besides AGE and isomers, 81.1% of desired product, γ -glycidoxypropylmethyldiethoxysilane. Also present were two unexpected scrambled products: γ -glycidoxypropyldimethyl(ethoxy)silane (1.10% by GC) and γ -glycidoxypropyltriethoxysilane (1.24% by GC). GC–MS data of the above mixture support the structures of the product and two scrambled side-products.

Hydrosilylation of 1 and 2 in a Larger-Scale Reactor. To a jacketed Hastelloy-C reactor, equipped with agitator,

temperature probe, condenser, and nitrogen purge, was added 391 lb [177.7 kg] (1559 mol) of allyl glycidyl ether (AGE), followed by 151 mL (15 ppm Pt) of 10% CPA catalyst solution and 0.36 lb [164 g] (470 ppm) of acetic acid promoter. The reactor contents were heated to 80 °C. Methyldiethoxysilane (370 lb [168.2 kg], 1255 mol) was then metered in at such a rate as to keep the reactor temperature between 80 and 90 °C. After completion of reaction: about 3.5 h of silane addition and a 1 h hold, a majority of the excess AGE/isomers was stripped to give a crude GC yield of 86.3% desired hydrosilylation product. GC analysis also showed 2.53% γ -glycidoxypropyldimethyl(ethoxy)silane and 2.95% γ -glycidoxypropyltriethoxysilane. GC–MS data of the above mixture again support the structures of the product and two side-products.

Hydrosilylation of 1 and 2 under Inverse Conditions. To a 250 mL four-neck round-bottom flask, equipped with stir bar, thermocouple probe, condenser, addition funnel, and nitrogen inlet/outlet, were added 67.0 g (0.52 mol) of methyldiethoxysilane, 78 μL (15 ppm Pt) of 10% CPA solution (CPA), and 90 μL (650 ppm) of acetic acid. The mixture was then heated to 85 °C. AGE (70.8 g, 20% excess at 0.62 mol), which had been charged to the addition funnel, was then added dropwise to the heated mixture at such a rate as to keep the pot temperature between 85 and 90 °C. After AGE addition completion (approximately 80 min), the reaction was then heated at 85 °C for 30 min. GC analysis of the crude reaction mixture showed complete conversion of the methyldiethoxysilane. GC analysis also showed, besides AGE/isomers, 75.3% of desired product, γ -glycidoxypropylmethyldiethoxysilane. Again present, although in smaller amounts, were the two unexpected scrambled products γ -glycidoxypropyldimethyl(ethoxy)silane (0.16% by GC) and γ -glycidoxypropyltriethoxysilane (0.36% by GC).

Hydrosilylation of 1 and 2 under Continuous Conditions. When the hydrosilylation reaction between methyldiethoxysilane and allyl glycidyl ether was run in a continuous mode (continuous hydrosilylation with recycling⁹) by co-feeding allyl glycidyl ether and excess methyldiethoxysilane to a reactor and recycling the excess methyldiethoxysilane, both exchanged precursors, $\text{Me}_2(\text{EtO})\text{SiH}$ and $(\text{EtO})_3\text{SiH}$, were observed in the recycle stream. Their combined levels ranged from approximately 5% to greater than 20% of the recycled methyldiethoxysilane stream. In addition, the crude product stream also contained steadily increasing amounts of exchanged hydrosilylation products, as the reaction time increased. The level of γ -glycidoxypropyldimethylethoxysilane, for example, increased from approximately 0.5% to more than 2% relative to 70–78% of the expected γ -glycidoxypropylmethyldiethoxysilane. GC–MS data of the above mixture support the structures of the product and two scrambled side-products.

Hydrosilylation of (1) with Cyclohexene (8) (Scheme 4). To a 50 mL four-neck round-bottom flask, equipped with stir bar, thermocouple probe, condenser, addition funnel, and nitrogen inlet/outlet, was added 5.16 mL (4.19 g, 0.05 mol)

(8) Filipkowski, M. A.; Petty, H. E.; Schilling, C. L., Jr.; Westmeyer, M. D. U.S. Patent 6,166,238, 2000.

(9) Schilling, C. L., Jr.; Burns, P. J.; Ritscher, J. S.; Bowman, M. P.; Childress, T. E.; Powell, M. P.; Graban, E. M. U.S. Patent 6,015,920, 2000.

of cyclohexene. A 10% excess of the raw material was used in the preparation. A solution of 10% chloroplatinic acid in ethanol (CPA, 6.56 μL , 55 ppm Pt) catalyst and 7.56 μL (630 ppm) of acetic acid promoter were added to the cyclohexene in the reaction vessel. The mixture was then heated to 90 °C. Methyl-diethoxysilane 6.82 mL (5.65 g at 95% or 5.37 g, 0.04 mol), which had been charged to the addition funnel, was then slowly added dropwise to the heated mixture. After silane addition completion (about 15 min), the reaction was heated at 90 °C for 60 min. GC along with GC–MS analysis showed, besides cyclohexene and methyl-diethoxysilane, the two unexpected scrambled (6,7) products in trace amounts (<1%) and a molecular peak corresponding to the hydrosilylation adduct of cyclohexene and dimethylethoxysilane (6). GC–MS data of the above mixture support the structures of the product two scrambled side-products and the hydrosilylation product.

Hydrosilylation of (1) and 1-Octene (12) (Scheme 5).

To a 100 mL three-neck round-bottom flask, equipped with stir bar, thermocouple probe, condenser, addition funnel, and nitrogen inlet/outlet, was added 19.3 g (0.169 mol) of 1-octene. An excess of the raw material was used as olefin isomerization may occur. A solution of 10% chloroplatinic acid in ethanol (CPA, 11 μL , 17 ppm Pt) catalyst was then added to the 1-octene. The mixture was then heated to 90 °C. Methyl-diethoxysilane (19.6 g, 0.143 mol), which had been charged to the addition funnel, was then added dropwise to the heated mixture. The pot temperature was kept between 100 and 103 °C throughout the addition (about 25 min). After addition, the reaction was then heated at 90 °C for 1 h. GC analysis showed, besides 1-octene and isomers, 80.4% of desired product, octylmethyl-diethoxysilane. Also present were two unexpected scrambled products: octyldimethyl-(ethoxy)silane (3.53% by GC) and octyltriethoxysilane (4.07% by GC). GC–MS Data of the above mixture support the structures of the product and two scrambled side-products.

Hydrosilylation of (1) and 2,3-Dimethyl-2-butene (16) (Scheme 6).

To a 25 mL three-neck round-bottom flask, equipped with stir bar, thermocouple probe, condenser, addition funnel, and nitrogen inlet/outlet, was added 3.68 mL (2.61 g, 31 mmol, 1.3 equiv) of 2,3-dimethyl-2-butene. A solution of 10% chloroplatinic acid in ethanol (CPA, 3.9 μL , 25 ppm Pt) catalyst and 4.5 μL (650 ppm) of acetic acid promoter are added to the AGE in the reaction vessel. The mixture was then heated between 68 and 72 °C. Methyl-diethoxysilane (4.04 mL, 3.35 g, 23 mmol, 1 equiv), which had been charged to the addition funnel, was then slowly added dropwise to the heated mixture at temperatures

between 67 and 73 °C. After silane addition completion (about 20 min), the reaction was then heated at 73 °C for a total of 5 h. GC analysis showed, besides mostly the two starting materials, trace amounts (<1%) of dimethylethoxysilane, triethoxysilane and the 2,3-dimethyl-2-butene/dimethylethoxysilane hydrosilylation product. These assignments were made using GC–MS data of the reaction mixture, which supports the structures of the rearranged silanes.

Hydrosilylation of (1) and Eugenol (20) (Scheme 7).

To a 25 mL three-neck round-bottom flask, equipped with stir bar, thermocouple probe, condenser, addition funnel, and nitrogen inlet/outlet, was added 5.20 g (4.88 mL, 31.7 mmol) of eugenol. A 30% excess of this raw material was used in the preparation, as isomerization of eugenol occurs in the presence of heat and platinum catalyst. A solution of 10% chloroplatinic acid in ethanol (CPA, 3.9 μL , 25 ppm Pt) catalyst and 4.5 μL (500 ppm) of acetic acid promoter were added to the eugenol in the reaction vessel. The mixture was then heated to 85 °C. Methyl-diethoxysilane (4.0 mL, 3.35 g, 25.0 mmol), which had been charged to the addition funnel, was then added dropwise to the heated mixture at such a rate as to keep the pot temperature between 85 and 90 °C. After silane addition completion (about 30 min), the reaction was then heated at 85 °C for 30 min. GC analysis showed, besides AGE and isomers, 73.2% of normal product, 3-(4-hydroxy-3-methoxyphenyl)propylmethyl-diethoxysilane. Also present in trace amounts was an unexpected scrambled product with the dimethylethoxysilane group, whose structure was supported by GC–MS data of the above mixture.

Hydrosilylation of Methyl-dimethoxysilane and Vinyl-cyclohexene Monoxide (Scheme 8).

When the hydrosilylation reaction between methyl-dimethoxysilane and vinyl-cyclohexene monoxide was run by adding the former to a 20% molar excess of the latter at 90 °C, followed by a 1 h hold at 90 °C after completion of the addition, using 10 ppm of platinum as a solution in ethanol, the alkyl/alkoxy group exchange reaction hydrosilylation products were observed by GC at combined levels of 2.4–3.4% relative to the expected methyl-diethoxysilane hydrosilylation product at 82–84%.

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