

New Routes to Phenylsilicones

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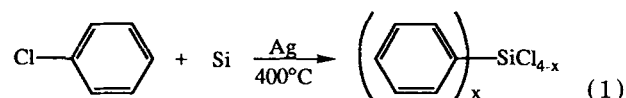
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SYNOPSIS

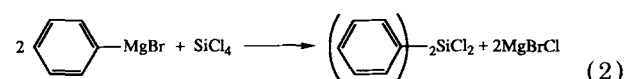
Two alternative nonhalogen routes for the synthesis of phenylsilanes have been explored. In the first method, 2,3-dimethylbutadiene is reacted with divinyltetramethyldisiloxane via a Diels–Alder reaction. The product can then be aromatized. In the second method, cyclohexadiene undergoes hydrosilylation and the resultant product can be aromatized using palladium on carbon with nitrobenzene as an electron acceptor. Phenylsilicones can be prepared in a single step in which a silicone hydride fluid and cyclohexadiene are refluxed in the presence of Pt/C (platinum on carbon) and nitrobenzene. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

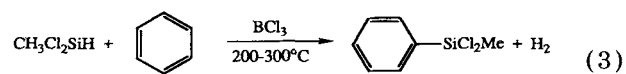
Phenylsilicones are useful as heat-transfer fluids and greases and in other applications where thermal stability is required.¹ Currently, phenylchlorosilanes, which are subsequently hydrolyzed to phenylsiloxanes, are prepared by one of three methods²: Via the direct process route, chlorobenzene is reacted with silicon metal at 400°C in the presence of a silver catalyst according to eq. (1):



In the second method, the Grignard reagent, phenylmagnesium bromide, is reacted with silicon tetrachloride [eq. (2)]:



The third method, the Barry Brewer process, involves the reaction of methylchlorosilane and benzene using boron trichloride as the catalyst [eq. (3)]:



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All the above methodologies for the synthesis of phenylsilicones have one major drawback, namely, the possibility of concomitant evolution of PCBs during synthesis.

Faltynek and co-workers explored an alternate route to phenylsilicones.³ They were able to utilize transition metals to mediate aryl transfers to silicon. Ruthenium, rhodium, palladium, and platinum halide complexes were found to be active catalysts. Unfortunately, the reaction rate was quite slow.

Thus, we began a program to identify alternative nonhalogen routes to phenylsilicones. The results of our investigation are described herein.

EXPERIMENTAL

Nitrobenzene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, 2,3-dimethylbutadiene, maleic acid, tetralin, cumene, cyclohexene, dichlorodicyanoquinone, trifluoromethane, sulfonic acid, platinum on carbon, palladium on carbon, platinum on alumina, Wilkinson's catalyst, and platinum black were obtained from Aldrich and used without further purification.

Triethylsilane, tetramethyldisiloxane, and diphenyltetramethyldisiloxane were obtained from Hüls America. A silicone hydride fluid containing 0.15% hydride and platinum divinyltetramethyldisiloxane (Karstedt's catalyst) were obtained from GE Silicones.

Gas Chromatography Analysis (GC)

Reactions were monitored by GC using a Shimadzu GC9A equipped with a 6 ft SE-30 column and flame ionization detector.

Gas Chromatography–Mass Spectrometry Analysis (GC–MS)

Reaction mixtures were analyzed by GC–MS to aid in identification of the peaks observed by gas chromatography. A Jeol SX-102 double-focusing mass spectrometer set to a mass resolution of 1000 with a scan rate of 1 spectrum per second was used for the analysis. A 200 eV chemical ionization (220°C) was employed with isobutane as the reagent gas. GC data was obtained with a temperature program on the J&W Scientific DB-1 GC column (30 m long with an i.d. of 0.32 mm, coated to a thickness of 1.0 μm) from 10°C (hold 1.5 min) to 270°C at 10°C/min.

Gel Permeation Chromatography (GPC)

Molecular weights and polydispersivities were determined using an HP1090 liquid chromatograph equipped with two PLgel 5 micron Mixed-D 300 \times 7.5 mm columns. Calibration was performed using polystyrene standards in conjunction with a silicone broad standard ($M_w = 85,470$; $M_n = 48,700$; from Hüls America). Chloroform was used as the eluent with an HP1047A refractive index detector.

Nuclear Magnetic Resonance Spectroscopy

^1H -NMR of reaction mixtures were acquired in a GE model QE-300 NMR spectrometer at 300.15 MHz. ^{13}C -NMR were recorded in a Varian 300 NMR spectrometer at 75.4 MHz.

Reaction of 2,3-Dimethyl-1,4-Butadiene with Divinyltetramethyldisiloxane

A 50 mL Parr bomb was charged with divinyltetramethyldisiloxane (4.8 g, 0.016 mol) and 2,3-dimethylbutadiene (6 g, 0.073 mol) and heated at 160°C for 24 h. After completion of the reaction, the products were monitored by GC and the identity confirmed by GC–MS. The product was collected by fractional distillation at 120°C/1 Torr and was 96% pure by GC.

Polymerization of Diphenyltetramethyldisiloxane with Octamethylcyclotetrasiloxane

A round-bottom flask was charged with octamethylcyclotetrasiloxane (1.5 g, 0.005 mol), diphenyltetramethyldisiloxane (0.35 g, 0.001 mol), and trifluoromethane sulfonic acid (10 μL). The reaction was stirred for 1 h, after which time MgO (0.5 g, 0.125 mol) was added to quench the reaction. The mixture was filtered and then analyzed by GPC.

Hydrosilylation of 1,3-Cyclohexadiene with Triethylsilane

A two-neck, round-bottom flask equipped with stir bar, reflux condenser, gas inlet, and pressure equalizing addition funnel was charged with 1,3-cyclohexadiene (8.0 g, 0.1 mol) and Karstedt's catalyst (10 μL). Then, the mixture was refluxed for 1 h. The product was collected by distillation at 60°C under vacuum. The structure was verified by ^1H -NMR and GC–MS.

Reaction of Cyclohexenyltriethylsilane with HCl

Cyclohexenyltriethylsilane (0.1 g, 0.0005 mol) was dissolved in chloroform (2 mL) and gaseous HCl was bubbled through the solution for 30 s. GC analysis of the reaction indicated the presence of cyclohexene and triethylchlorosilane.

Hydrosilylation of Tetramethyldisiloxane with 1,3-Cyclohexadiene

A two-neck, round-bottom flask was charged with 1,3-cyclohexadiene (16 g, 0.2 mol) and chloroplatinic acid (0.001 g, 2.6 μmol). Tetramethyldisiloxane (13.6 g, 0.1 mol) was added dropwise. An exotherm was observed. After 1 h, the product was distilled at 90°C *in vacuo*. The product identification was verified by GC–MS.

Attempted Dehydrogenation of Bis(dimethylcyclohexenyl)disiloxane with Wilkinson's Catalyst

A round-bottom flask was charged with bis(dimethylcyclohexenyl)disiloxane (1.0 g, .0035 mol), tris(triphenylphosphine)rhodium (1) chloride (0.02 g, 21.6 μmol), and 5 mL cumene. The mixture was refluxed overnight, after which time the cumene was removed by distillation. ^1H -NMR indicated that no dehydrogenation had occurred.

Dehydrogenation of Bis(dimethylcyclohexenyl)disiloxane Using Pd/C

A round-bottom flask was charged with bis(dimethylcyclohexenyl)disiloxane (2 g, 0.007 mol) and palladium on carbon (5% Pd, 0.02 g). The mixture was refluxed overnight under N₂. ¹H-NMR of the resultant mixture indicated that the starting material had undergone disproportionation.

Attempted Dehydrogenation of Bis(dimethylcyclohexenyl)disiloxane in the Presence of Maleic Acid

A round-bottom flask was charged with bis(dimethylcyclohexenyl)disiloxane (1 g, 0.0035 mol), Pd/C (5% Pd, 0.01 g), maleic acid (1.6 g, 0.013 mol), and 5 mL cumene. The mixture was refluxed overnight. GC analysis of the resultant mixture indicated large amounts of decomposition.

Conversion of Cyclohexene to Benzene Using Pt/Al₂O₃

A quartz tube packed with Pt/Al₂O₃ was attached to a Schlenk flask and capped with a rubber septum. The catalyst bed was heated to 475°C under hydrogen. Cyclohexene was then passed through the column under nitrogen and the product was collected in the Schlenk flask. ¹H-NMR of the product indicated 100% conversion to benzene (86% yield) and cyclohexane (14% yield).

Attempted Dehydrogenation of Bis(dimethylcyclohexenyl)disiloxane Using Pt/Al₂O₃

As per the above, bis(dimethylcyclohexenyl)disiloxane was passed at 350°C through an activated bed of Pt/Al₂O₃. The analysis products indicated that gross decomposition with Si—C bond cleavage had occurred.

Attempted Dehydrogenation of Bis(dimethylcyclohexenyl)disiloxane Using Pt Black and Cumene

A round-bottom flask was charged with bis(dimethylcyclohexenyl)disiloxane (1 g, 0.035 mol), Pt black (0.3 g), and cumene (5 mL). The mixture was allowed to reflux overnight. The catalyst was removed by filtration and the cumene by distillation. ¹H-NMR and GC analysis indicated complete conversion to bis(dimethylcyclohexyl)disiloxane (50%) and diphenyltetramethyldisiloxane (50%).

Dehydrogenation of Cyclohexenyltriethylsilane with Pd/C in the Presence of Nitrobenzene

A 50 mL round-bottom flask was equipped with a reflux condenser, gas inlet with cyclohexenyltriethylsilane (2.0 g, 0.01 g), Pd/C (10% Pd, 0.2 g), and nitrobenzene (20 mL). The mixture was heated to 175°C with a stream of nitrogen slowly bubbling through the solution. After 24 h, the products were analyzed by GC. There was approximately 70% conversion to phenyltriethylsilane.

Hydrosilylation and Dehydrogenation of 1,3-Cyclohexadiene and Triethylsilane Mixtures

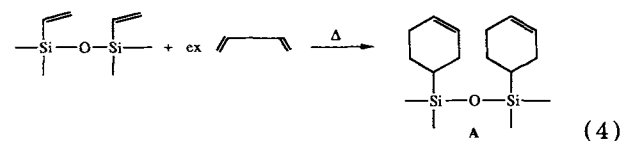
A two-neck, round-bottom flask with a dry-ice condenser and spin bar was charged with 1,3-cyclohexadiene (2 g, 0.025 mol), Pt/C (1% Pt, 2.0 g), and nitrobenzene (20 g). Triethylsilane (2.9 g, 0.025 g) was added dropwise. The mixture was heated to 50°C overnight. GC analysis of the mixture indicated that both hydrosilylation and dehydrogenation had occurred.

Reaction of Silicone Hydride Fluid with Cyclohexadiene and Nitrobenzene

A 100 mL round-bottom flask was charged with 1,3-cyclohexadiene (5 g, 0.0625 mol), silicone hydride fluid (7.75 g), and Pt/C (5%, 0.14 g). The mixture was heated to 110°C overnight. Then, nitrobenzene (30 mol) was added and the mixture refluxed overnight. An aliquot was analyzed by ²⁹Si-NMR and showed that complete hydrosilylation and partial dehydrogenation had occurred.

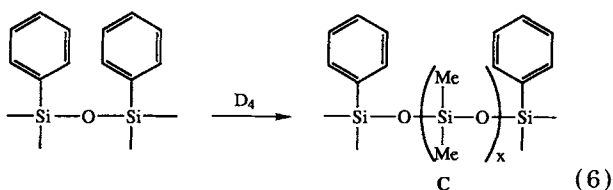
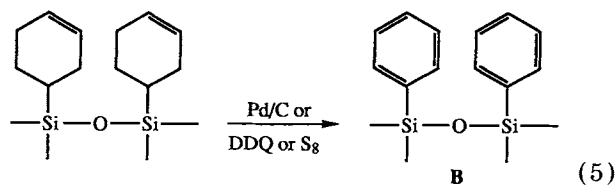
RESULTS AND DISCUSSION

Two methodologies were explored as potential alternative routes to phenylsilanes. The reaction sequences can be envisaged as follows: In the first potential method, vinyl-containing siloxanes could be reacted with butadienes to form cyclohexenylsiloxanes by a Diels–Alder reaction [eq. (4)]:



This product could potentially be dehydrogenated by a variety of routes to lead to phenyldisiloxanes. The phenyldisiloxane thus produced could then be

equilibrated with octamethylcyclotetrasiloxane (D_4) using trifluoromethane sulfonic acid as the catalyst to give phenylsilicone polymers [eqs. (5) and (6)]:

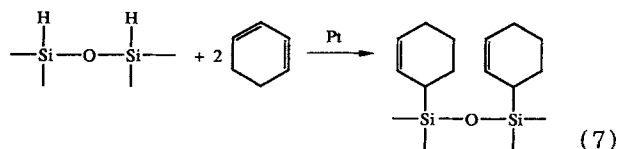


To explore this synthetic route, divinyltetramethyldisiloxane was reacted with excess 2,3-dimethylbutadiene in a Parr bomb at 160°C for 24 h. GC analysis indicated the presence of two silicon-containing products, bis(dimethylcyclohexenyldimethyl)disiloxane and the monodimethylcyclohexenyl vinyltetramethyldisiloxane (Fig. 1). The desired product was easily purified by distillation and verified by GC-MS.

The product was then dehydrogenated with Pd/C to give a mixture of phenyltetramethyldisiloxane, dicyclohexyltetramethyldisiloxane, and cyclohexylphenyltetramethyldisiloxane (Fig. 2). The product distribution is indicative of a disproportionation mechanism with this catalyst. No further effort was made to optimize this reaction.

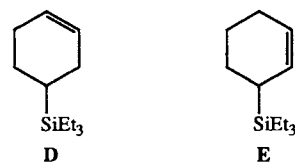
To examine the viability of the third reaction in this sequence, diphenyltetramethyldisiloxane was equilibrated with D_4 using trifluoromethane sulfonic acid. After allowing the equilibration to proceed for 1 h, the reaction was quenched with magnesium oxide. GPC indicated that the polymer formed in this reaction had mp = 1164 with a dispersivity of 1.8 (Fig. 3).

A second approach for the synthesis of phenyl-containing silicones from silicone hydrides can be delineated as follows: Tetramethyldisiloxane can be reacted with two equivalents of 1,3-cyclohexadiene using a platinum hydrosilylation catalyst such as Karstedt's catalyst according to eq. (7):

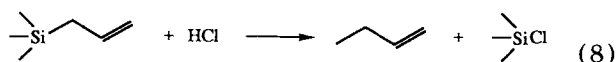


The dicyclohexenyldimethylsiloxane thus formed can then be dehydrogenated and finally equilibrated with D_4 to give phenyl-terminated silicone polymers as described above (*vide supra*).

There are few examples of the hydrosilylation of internal olefins.⁴ However, hydrosilylation of 1,3-cyclohexadiene with either triethylsilane or tetramethyldisiloxane proceeded easily and in good yield. The hydrosilylation did not proceed using 1,4-cyclohexadiene as the substrate, which suggests that the conjugation of 1,3-cyclohexadiene is responsible for the relative ease by which the reaction proceeds. The reaction could occur by either 1,2 or 1,4 addition. Product D is obtained from 1,2 addition only, whereas product E could be obtained from either 1,2 or 1,4 addition. Unfortunately, neither ¹³C-NMR or ¹H-NMR could be used to conclusively determine whether the product had structure D or E:



However, reaction of the product with gaseous HCl in chloroform yielded cyclohexene and triethylsilylchloride, indicating that E was the product since only allylsilanes react with nucleophiles to cleave the silicon carbon bond, i.e., eq. (8):



The next step in the synthesis, namely, the dehydrogenation of the cyclohexenylsilicon compound, proved to be the most problematic. Many catalysts were explored including heterogeneous platinum catalysts and palladium catalysts, and Wilkinson's catalyst. Quinones were also tried in stoichiometric reactions. Reactions were also tried in the presence of electron acceptors such as maleic anhydride, tetralin, and nitrobenzene.

In the original experiments using Pt/C and Pd/C, triethylcyclohexenylsilane underwent disproportionation to yield 33% phenyltriethylsilane (see Fig. 4). Analogous results were obtained with bis(dimethylcyclohexenyl)disiloxane. DDQ was also tried as a dehydrogenating agent. Although it was an effective method, workup and recovery of the DDQ was unwieldy.

Pt/ Al_2O_3 was shown by Reiker et al.⁶ to promote the conversion of cyclohexene to benzene. This re-

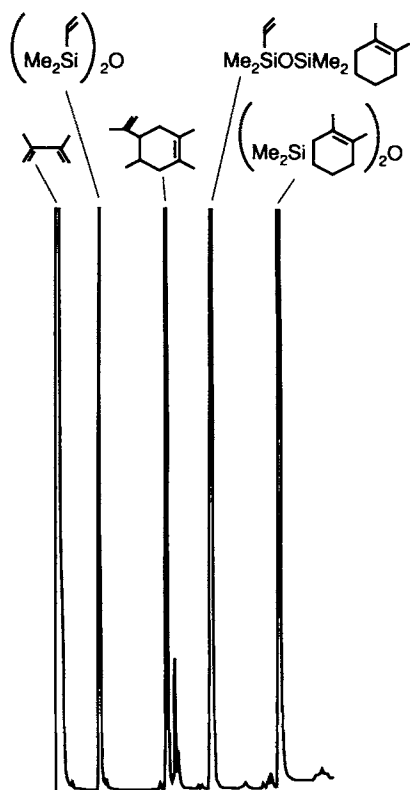
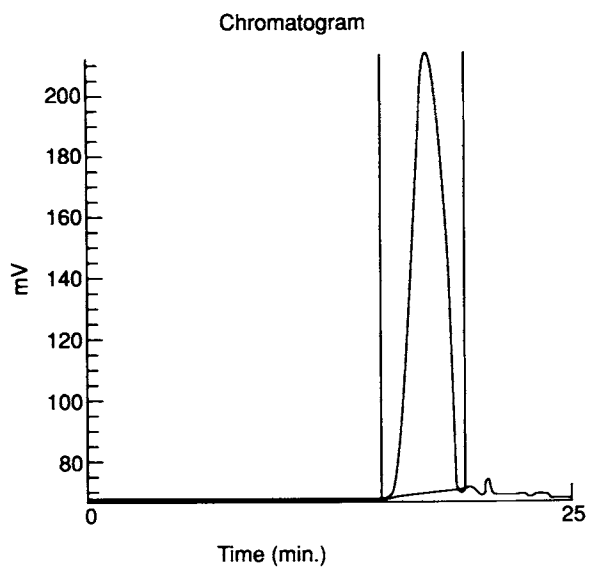
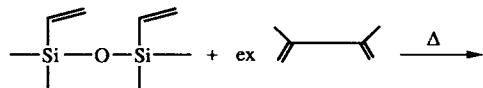
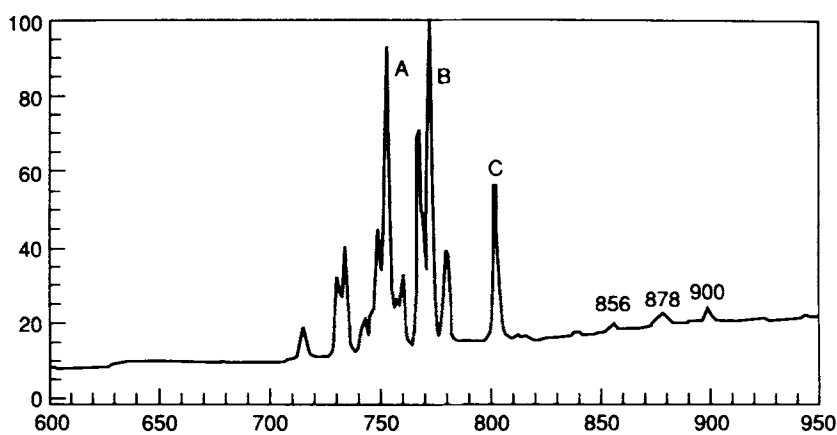
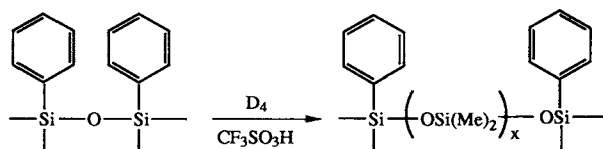


Figure 1 Gas chromatogram of the reaction products of



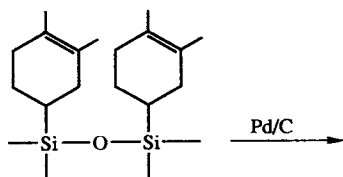
Mn = 868 Mp = 1164
 Mw = 1556 Mv = 0
 Mz = 2751 D = 1.7921

Figure 3 Gel permeation chromatogram of the reaction products of



- Legend**
- A
 - B
 - C

Figure 2 Reconstructed gas chromatogram of the reaction products of



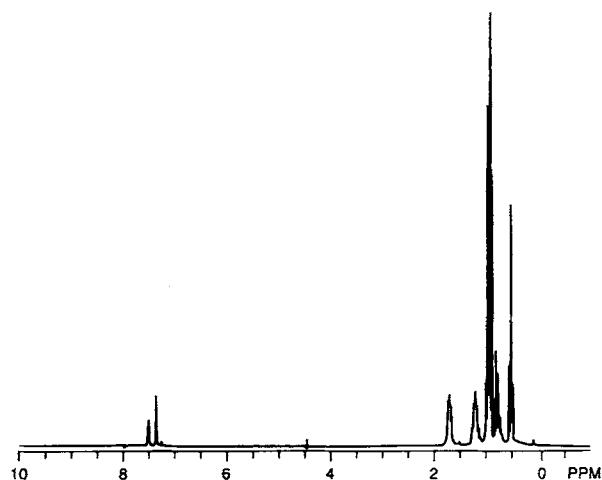
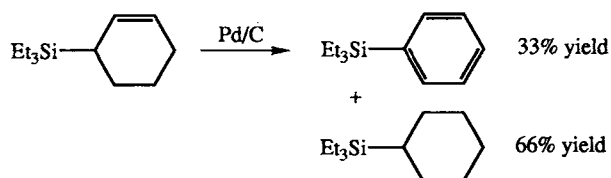


Figure 4 $^1\text{H-NMR}$ spectrum of the reaction products of



sult was verified by us. However, passage of either cyclohexenyltriethylsilane or bis(dimethylcyclohexenyl)disiloxane through a column of $\text{Pt}/\text{Al}_2\text{O}_3$ at 470°C resulted only in decomposition.

A variety of hydrogen acceptors were screened. Neohexene, tetralin, and maleic acid had little if any effect. However, dehydrogenation of the cyclohexenyltriethylsilane proceeded to 75% conversion using Pd/C in nitrobenzene (see Fig. 5).

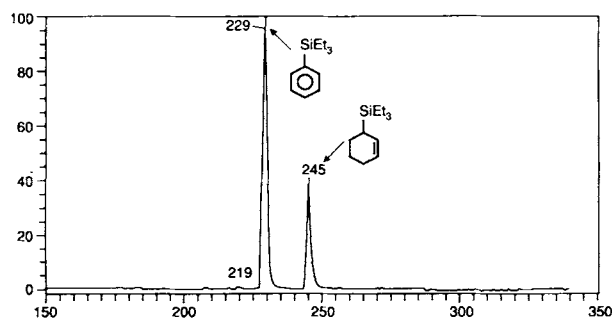


Figure 5 Reconstructed gas chromatograph of the reaction products of

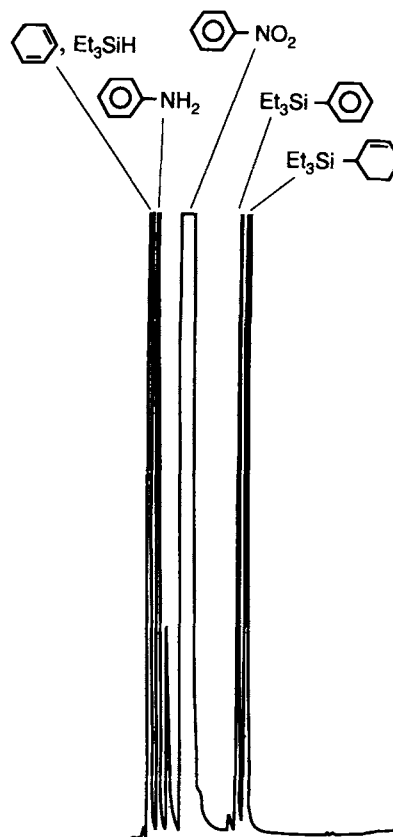
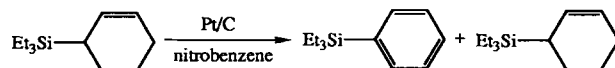
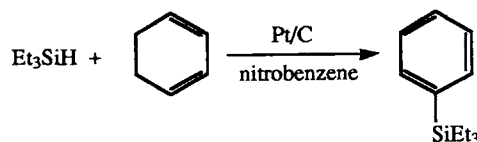
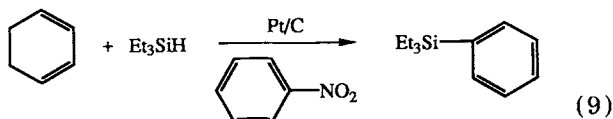


Figure 6 Gas chromatogram of the reaction products of



We then explored the possibility of hydrosilylation/dehydrogenation in one step according to eq. (9):



After allowing the reaction to reflux for 1 day, GC indicated the presence of two products, cyclohexenyltriethylsilane and phenyltriethylsilane (Fig. 6). Next, the possibility of preparing phenylsilicone polymers directly from silicone hydride fluids and cyclohexadiene was explored. A hydride fluid was reacted with two equivalents of cyclohexadiene in nitrobenzene using Pt/C as the catalyst. The reaction was monitored by $^{13}\text{C-NMR}$ (Fig. 7). In the

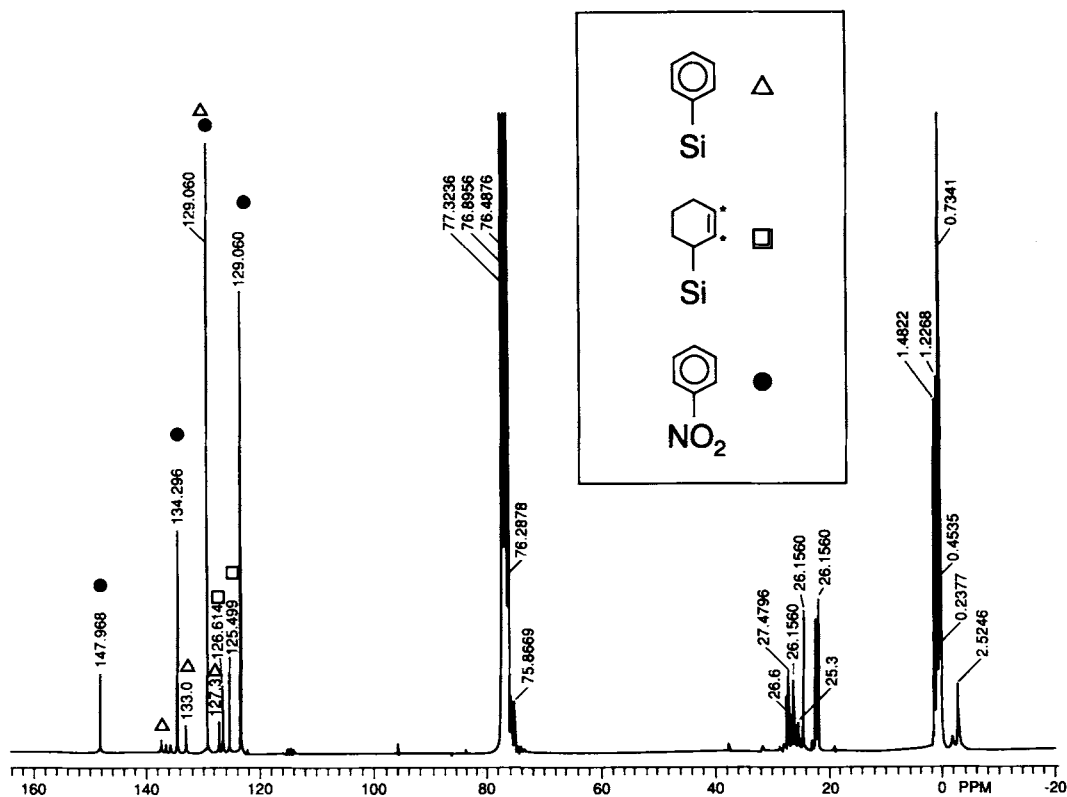
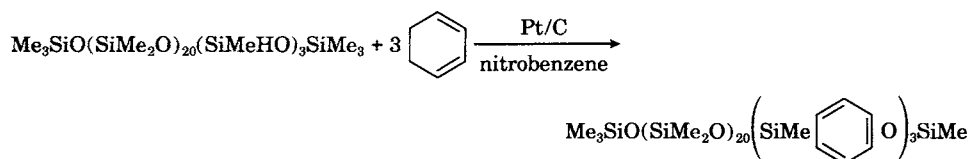


Figure 7 ^{13}C -NMR spectrum of the reaction



olefinic region, peaks were assigned to phenyl carbons, nitrobenzene, and the alkene carbons of cyclohexenyl groups. Thus, phenylsilicones could be directly prepared from silicone hydride polymers. No attempts were made to separate the products or increase the yield of the reaction.

CONCLUSION

Two new routes to phenylsilicones have been discovered that do not require halogenated starting materials or catalysts and thus eliminate PCB formation during synthesis. Although the methodology has not been optimized, we have shown that phenylsilicones can be prepared in a single step via hydrosilylation/dehydrogenation reactions.

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