

HYDROSILOXANE ADDITIONS AND ISOMERIZATIONS OF 2- AND 1-PROPENYL BENZYL ETHERS

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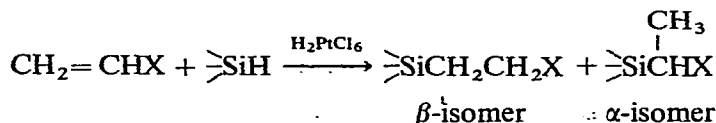
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SUMMARY

Platinum-catalyzed hydrosilation reactions of allyl or propenyl benzyl ethers yield both γ - and β -silylated propyl benzyl ethers. The γ -isomer predominates in each case, implicating propenyl-allyl isomerization in the much slower reactions of propenyl benzyl ether. The allyl-propenyl isomerization is also observed under the reaction conditions. It appears that β -isomers may arise from hydrosilation of propenyl benzyl ether or from non-terminal hydrosilation of allyl benzyl ether.

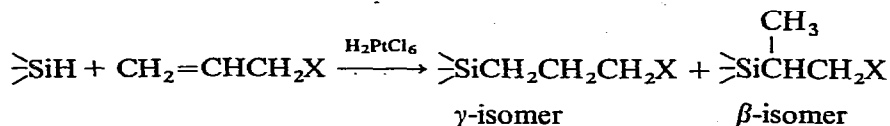
INTRODUCTION

The addition of silicon hydrides to olefinic bonds in the presence of chloroplatinic acid is well documented in the papers of Speier and coworkers¹⁻¹⁰. The voluminous literature of silicon hydride additions to multiple bonds has been reviewed¹¹⁻¹³. Additions to hydrocarbon olefins have been investigated in detail with regard to isomer distributions of products and isomerizations of starting olefins^{2,5-10,14-16}. Functional vinyl monomers, such as styrene, acrylates, and acrylonitrile, are known to give both β - and α -isomers upon hydrosilation

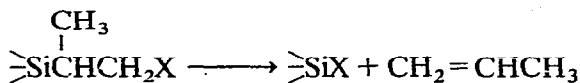


in the presence of chloroplatinic acid^{3,9,11-13}. Similar information concerning allyl compounds, particularly allyl ethers, seems lacking in the open literature. Hydro-siloxane additions to allyl ethers are of considerable commercial importance in the preparation of non-hydrolyzable silicone-polyether copolymer surfactants¹⁷.

In general, the reported products from hydrosilations of allyl compounds have been γ -substituted propylsilicon derivatives. β -Substituted propylsilicon derivat-



ives have been suspected, but not confirmed. The generation of propylene from hydrosilations of allyl esters and allyl halides has been proposed to result from decomposition of intermediate β -adducts, which were not isolated^{1,4,6,18,19}.



2-(Trichlorosilyl)-1-chloropropane [$\text{Cl}_3\text{SiCH}(\text{CH}_3)\text{CH}_2\text{Cl}$], however, was recovered unchanged after use as solvent for the addition of trichlorosilane to allyl chloride, casting doubt on the β -adduct decomposition mechanism⁶ and implicating propylene formation from some platinum-complexed species.

RESULTS AND DISCUSSION

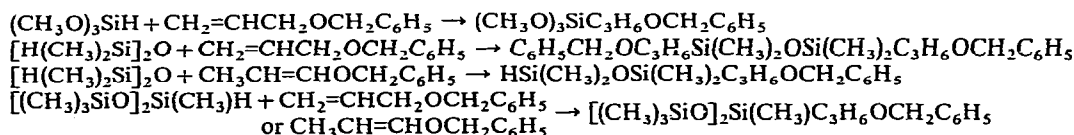
In the interest of studying the hydrosilation of allyl ethers, model reactions of trimethoxysilane, 1,1,3,3-tetramethyldisiloxane and 1,1,1,3,5,5,5-heptamethyltrisiloxane were run with 2-propenyl benzyl ether (hereinafter referred to as allyl benzyl ether), and 1-propenyl benzyl ether (hereinafter referred to as propenyl benzyl ether). Both β - and γ -substituted propylsiloxanes were produced in each reaction. Reaction conditions (which differ somewhat due to large rate differences), products, yields, and γ/β isomer ratios, are listed in Table 1.

TABLE 1

HYDROSILOXANE ADDITIONS TO ALLYL AND PROPENYL BENZYL ETHERS^a

Siloxane	Olefin ^b	Time (h)	Temp. (°C)	Stoich. ^c	Cat. ^d	Yield (%)	γ/β
$(\text{CH}_3\text{O})_3\text{SiH}$	ABE	1	80-107	1.8/1	1.0×10^{-2}	63	39.0
$(\text{CH}_3\text{O})_3\text{SiH}$	PBE	101	100-123	1.8/1	7.0×10^{-2}	0 ^e	
$[\text{H}(\text{CH}_3)_2\text{Si}]_2\text{O}$	ABE	$\frac{1}{2}$	100-120	0.5/1.47	0.5×10^{-2}	98	19.0
$[\text{H}(\text{CH}_3)_2\text{Si}]_2\text{O}$	PBE	68	100-136	0.5/1.13	6.2×10^{-2}	22	2.0
$[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{H}$	ABE	1	100-122	1/1	0.4×10^{-2}	80	19.0
$[(\text{CH}_3)_3\text{SiO}]_2\text{Si}(\text{CH}_3)\text{H}$	PBE	45	115	1/1	7.0×10^{-2}	38	4.0

^a Additions were run without solvents. Reduced platinum appeared in PBE additions due to long reaction times. Additions to ABE were clear and homogeneous. ^b ABE is allyl benzyl ether; PBE is propenyl benzyl ether. ^c Ratio of siloxane to olefin. ^d Weight % of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ of total reactants. ^e Only noticeable reaction was disproportionation of trimethoxysilane to tetramethoxysilane.



where $\text{>SiC}_3\text{H}_6\text{-}$ is $\text{>SiCH}_2\text{CH}_2\text{CH}_2\text{-}$ or $\text{>SiCH}(\text{CH}_3)\text{CH}_2\text{-}$

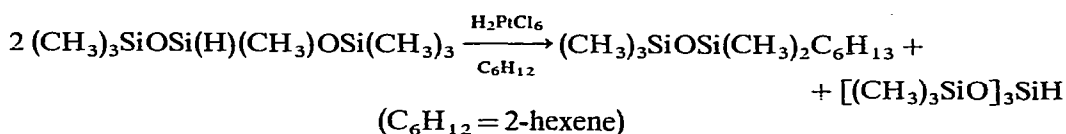
Three significant conclusions can be drawn from these experiments. First, hydrosiloxanes can add internally to propenyl ethers to form β -substituted propylsiloxanes. Second, propenyl ethers can isomerize to allyl ethers under these conditions to ultimately yield γ -substituted propylsiloxanes. The isomerization of allyl to propenyl also occurs under these conditions, such that the allyl-propenyl isomeriza-

tion is reversible. Under basic conditions, the isomerization of allyl to propenyl is regarded to be irreversible²⁰. Third, while the much lower γ/β ratios observed for propenyl benzyl ether additions *vs.* those of allyl benzyl ether implicate internal addition to the propenyl group, the possibility of β -addition of allyl groups is not eliminated. In fact, the reaction of trimethoxysilane and allyl benzyl ether yields some β -adduct (2.5%), while trimethoxysilane and propenyl benzyl ether yield none of either adduct. Also the amounts of β -isomer appearing in reactions of 1,1,3,3-tetra-methyltrisiloxane or 1,1,1,3,5,5,5-heptamethyltrisiloxane with allyl benzyl ether (about 5% in 1 h or less) *vs.* those of the corresponding reactions with propenyl benzyl ether (7–8% in 45–68 h) indicate that β -addition to allyl groups does occur.

The present results are consistent with initial hydride transfer within the complex, as previously proposed^{4,6,16,25}. If the X-group of the allyl compound can form a stable leaving group (or platinum ligand) such as a halide or acylate anion, it can be displaced by hydride attack to form propylene and ultimately the >SiX compound. If X cannot form a stable leaving group (or platinum ligand) as is the case with allyl or propenyl ethers, the complex either forms product irreversibly or reverts to an olefin-hydrosiloxane complex. Deuterium scrambling shows the hydride additions are reversible⁷, while the reaction with the silicon portion is not²¹.

It is of interest that $[\text{H}(\text{CH}_3)_2\text{Si}]_2\text{O}$ and propenyl benzyl ether gave largely monoadduct, while none was detected in the addition of $[\text{H}(\text{CH}_3)_2\text{Si}]_2\text{O}$ and allyl benzyl ether. Diadduct may have been present in the former case in small amounts but was not isolated. The reaction of 1,1,1,3,5,5,5-heptamethyltrisiloxane and allyl benzyl ether at a 1/1 molar ratio, yielded *cis*- and *trans*-propenyl benzyl ethers as the only recovered olefins, proving that isomerization of allyl to propenyl does occur in these reactions. Accordingly, an excess of one reactant was used in most other reactions.

The rearrangement of 1,1,1,3,5,5,5-heptamethyltrisiloxane as reported by Speier¹⁰ and shown below, also occurs in its reaction with propenyl benzyl ether. Although two lower boiling products were not isolated, one was identified as $[(\text{CH}_3)_3\text{SiO}]_3\text{SiH}$



by comparative and mixed VPC analyses using authentic $[(\text{CH}_3)_3\text{SiO}]_3\text{SiH}^*$. The other is presumably $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{C}_3\text{H}_6\text{OCH}_2\text{C}_6\text{H}_5$.

The structural assignment of the β -substituted propylsiloxane linkage is based on VPC, NMR and elemental analyses of distilled mixtures of isomeric products. Pure β - or γ -isomers were not isolated. The CH_3CH -grouping of the β -isomers appears as a singlet with fine splitting at 0.9–1.1 τ from external TMS (60 MHz, CCl_4), free from interference by the >SiCH_2 - and $-\text{CH}_2\text{CH}_2\text{O}$ - protons of the γ -isomers. The chemical shift between the methyl and methine protons is essentially zero, as no

* Authentic $[(\text{CH}_3)_3\text{SiO}]_3\text{SiH}$ was purchased from Marschallton Laboratories, West Chester, Pennsylvania.

better resolution was obtained at 220 MHz. The CH_3CH -group of $\text{CH}_3\text{CH}(\text{SiCl}_3)_2$ also appears as a singlet²². Integration values were corrected for ^{13}C satellites and spinning side bands.

EXPERIMENTAL

1,1,3,3-tetramethyldisiloxane was prepared by hydrolysis of dimethyl chlorosilane with cracked ice¹. Trimethoxysilane, 1,1,1,3,5,5,5-heptamethyltrisiloxane (both produced by Union Carbide), and the disiloxane were freshly distilled before use. Allyl benzyl ether was made by the method of Watanabe, *et al.*²³. The purity of all reactants was greater than 99% by VPC. All reactions were run in nitrogen atmospheres. VPC data was collected with an F & M 810 chromatograph using a $6' \times 3/16''$ column packed with 20% SE-30 on Chromosorb P, operated on a program of ambient to 250° at 20°/min. NMR spectra were recorded in CCl_4 on Varian A60A or 220 MHz spectrometers. The platinum catalyst was 4.0 wt. % $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in 1,2-dimethoxyethane. Microanalyses were performed by Galbraith Laboratories, Inc.

Propenyl benzyl ether

The dibenzyl acetal of propionaldehyde was prepared from benzyl alcohol (1530 g, 14.2 moles), and propionaldehyde (350 g, 6.0 moles) in 350 g of refluxing hexane, using 2.0 g *p*-toluenesulfonic acid, according to the method of Rottig and Liethen²⁴. When 108 g (100%) H_2O had collected, 0.6 g sodium methoxide was added to neutralize the catalyst. The product, b.p. 95–100° (1.0 mm) (1290 g), was identified by NMR and used without further purification. The acetal was thermally cracked at 185° in the presence of phenyl isocyanate to scavenge the benzyl alcohol formed, and the olefin ether distilled from the crude mixture. Pure product, b.p. 70° (2.0 mm) was shown to be 2/1 mixture of *cis/trans* isomers by NMR and VPC. (Found: C, 81.22; H, 8.18. $\text{C}_{10}\text{H}_{12}\text{O}$ calcd.: C, 81.08; H, 8.11 %.)

Reaction of trimethoxysilane and allyl benzyl ether

The olefin (13.4 g, 0.09 mole) was added to the siloxane (20.0 g, 0.164 mole) containing 0.10 ml platinum catalyst at 50°. The temperature rose to 80° and was maintained at 80–95° by rate of addition. Reaction was heated at 107° for 1 h after addition, followed by vacuum distillation. *Cis*- and *trans*-propenyl benzyl ethers (2.0 g) were recovered, no attempt being made in this or succeeding experiments to recover the low boiling siloxane reactants. Product was isolated at 102–104° (0.7 mm) (15.3 g, 63% based on starting olefin), leaving 3.0 g of residue. The product, (trimethoxysilyl)propyl benzyl ether, contained 2.5% β -isomer by VPC and NMR. (Found: C, 57.76; H, 8.32; Si, 10.69. $\text{C}_{13}\text{H}_{22}\text{O}_4\text{Si}$ calcd.: C, 57.78; H, 8.15; Si, 10.37 %.)

Reaction of trimethoxysilane and propenyl benzyl ether

The olefin (13.4 g, 0.09 mole), siloxane (20.0 g, 0.164 mole), and platinum catalyst (0.10 ml initially, 0.60 ml added incrementally during reaction) were heated at 100–123° for 101 h. The only reaction occurring, as monitored by VPC, was disproportionation of trimethoxysilane to tetramethoxysilane. Neither β - or γ -adduct was detected.

Reaction of 1,1,3,3-tetramethyldisiloxane and allyl benzyl ether

The siloxane (8.0 g, 0.06 mole) was added to the olefin (22.5 g, 0.152 mole) containing 0.05 ml platinum catalyst in 20 min. Cooling by water bath was necessary to keep temperature below 100°. Heat was applied to a final temperature of 120° for 25 min after addition. The product was neutralized with 0.5 g sodium bicarbonate, treated with Hyflo Super-Cel (Johns-Manville), filtered, and vacuum stripped at 100° (1.0 mm). The yield of diadduct was 98% (25.4 g). An analytical sample, b.p. 200° (1.0 mm) contained 5% β -propyl linkages by NMR. (Found: C, 67.11; H, 8.95; Si, 13.27. $C_{24}H_{38}O_3Si_2$ calcd.: C, 66.98; H, 8.84; Si, 13.02%.)

Reaction of 1,1,3,3-tetramethyldisiloxane and propenyl benzyl ether

The siloxane (8.0 g, 0.06 mole) and the ether (20.0 g, 0.135 mole) were heated at 100–130° for 68 h in the presence of 0.50 ml platinum catalyst. Workup as above and distillation yielded recovered olefins (14.0 g, 70%) at 60–71° (0.7 mm) and a mixture of monoadducts (3.6 g, 22% based on >SiH consumed) at 76–86°/1.0 mm. The γ/β ratio was 2/1 from VPC and NMR analyses. The pot residue (4.0 g) was largely undistilled monoadducts. (Found: C, 59.44; H, 9.07; Si, 19.97. $C_{14}H_{26}O_2Si_2$ calcd.: C, 59.57; H, 9.22; Si, 19.86%.)

Reaction of 1,1,3,3-tetramethyldisiloxane and propenyl benzyl ether

The olefin (32.5 g, 0.22 mole) was added to the siloxane (50.0 g, 0.22 mole) containing 0.10 ml platinum catalyst solution. Temperature increased from 50° to 122° during addition (12 min), and was held at 100° for 40 additional min. Workup as above yielded recovered olefin ethers, identified as only *cis*- and *trans*-propenyl benzyl ethers by NMR, and product (65.2 g, 80%) at 112–119° (0.12 mm) with a γ/β ratio of 19/1.

Reaction of 1,1,1,3,5,5,5-heptamethyltrisiloxane and propenyl benzyl ether

The siloxane (15.0 g, 0.07 mole) and the olefin were heated at 115° for 45 h in the presence of 0.35 ml platinum catalyst solution. Workup as above yielded 53% recovered olefins and 38% of the same γ - and β -adducts obtained above, in a 4/1 ratio by VPC and NMR. (Found: C, 54.97; H, 9.22; Si, 22.78. $C_{17}H_{34}O_3Si_3$ calcd.: C, 55.13; H, 9.19; Si, 22.70%.)

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