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Photoactivated telomerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane with hydrosilanes by Pt(acac)$_2$ and its competition with hydrosilylation addition

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Abstract

Telomerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane with hydrosilanes is facilitated by UV irradiation in the presence of Pt(acac)$_2$. When olefin is also present, photoactivated hydrosilylation competes with telomerization. The dependence of product distribution on the reactivity of the hydrosilanes and the olefins was studied. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: photoactivated; telomerization; hydrosilylation; 1,1,3,3-tetramethyl-1,3-disilacyclobutane; platinum(II) bis(β-diketonate).

Photoactivated hydrosilylation reactions have attracted interest since Boardman and Oxman discovered that platinum(II) bis(β-diketonate) may serve as an efficient photoactivated hydrosilylation catalyst.[1] Lewis subsequently reported on the photochemistry of such transition metal complexes,[2] as well as their catalytic behavior.[3] We discovered that platinum(II) acetylacetonate, Pt(acac)$_2$, also promotes UV induced ring opening polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDSCB).[4] We have now investigated what happens when hydrosilanes, olefins and silacyclobutanes coexist in a single system.

Irradiation (350 nm) of a degassed[5] equimolar solution of triethylsilane, vinyltriethylsilane and TMDSCB (0.5 M in CH_2Cl_2) in the presence of Pt(acac)$_2$ (5×10^{-4} M), results, after an induction period, in vigorous exothermic formation of hydrosilylation adduct **1**, *and* 'capped' ring-opened products **2** and **3** (Eq. 1).[6] Analysis of the residue by NMR after distillation also showed the presence of oligomers of TMDSCB.

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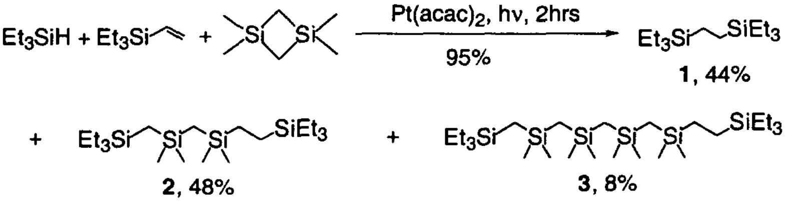
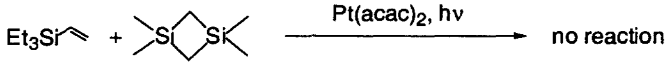
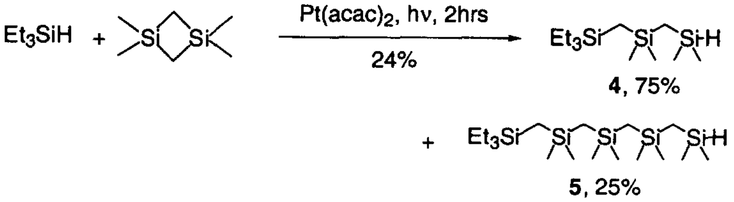


(1)

There is essentially no reaction between vinyltriethylsilane and TMDSCB under similar conditions (Eq. 2) while telomerization products **4** and **5** are formed from reaction of triethylsilane and TMDSCB (Eq. 3). Therefore, **2** and **3** are hydrosilylation adducts of **4** and **5** to vinyltriethylsilane, respectively.

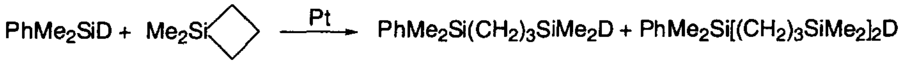


(2)



(3)

Platinum catalyzed thermal reactions of silacyclobutanes and disilacyclobutanes with silicon hydrides were first reported by Nametkin et al.[7] Studies with phenyldimethylsilane-*d* show the reaction involves ligand exchange between the two silicon atoms (Eq. 4).[8]

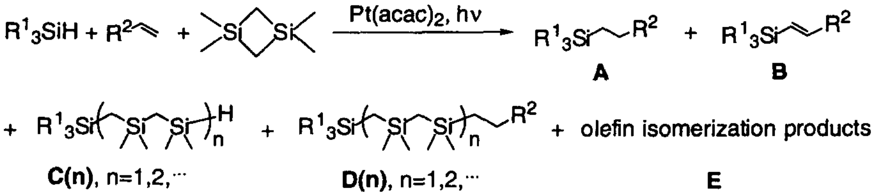


(4)

Alkyl silicon hydrides have also been effectively employed to control the molecular weight of poly(dimethylsilylenemethylene) that results from ring opening polymerization of TMDSCB by group VIII metal catalysts.[9]

The two photoactivated reactions, hydrosilylation and telomerization, compete efficiently to yield comparable quantities of products (see the reaction in Eq. 1); the reaction in Eq. 3 is the first example of analogous photoactivated interaction between a silicon hydride and a disilacyclobutane.

Reactions of TMDSCB with several different silicon hydrides and olefins were tested to explore the effect of starting material reactivity on product distribution (Table 1). We observed five different processes (Eq. 5): hydrosilylation addition (**A**), dehydrogenative silylation (**B**), telomerization (**C**), further hydrosilylation of olefin by the telomerization product (**D**) and isomerization of olefin (**E**). Tuning the reactivity of starting material results in wide product distribution, reflecting competition between the reactions.



(5)

Both electronic and steric effects are known to influence the reactivity of hydrosilanes in hydrosilylation reactions.[10] We find that bulky isopropyl substituents decrease reactivity, substantially lowering conversion of hydrosilanes and olefins. Moreover, dehydrogenative silylation plays an important role.[11]

Table 1
Photoactivated reactions of silicon hydride, olefin and TMDSCB[a]

Entry	R^1	R^2	Reaction Time (h)[b]	Conversion (%)[c]			Products (%)[d]						
				R^1_3SiH	$R^2CH=CH_2$	TMDSCB	**A**	**B**	**C** (1)	**C** (2)	**D** (1)	**D** (2)	**E**
1	iPr	Et_3Si	20	22	26	40	19	27	-	-	54	-	-
2	EtO	Et_3Si	2	91	90	17	97	-	-	-	3	-	-
3	Et	$(EtO)_3Si$	2	93	91	100	52	-	-	-	40	8	-
4	Et	Ph	2	66	64	100	27	-	-	-	44	29	-
5	Et	$COOCH_3$	8	72	25	100	39	-	14	10	23	14	-
6	Et	$(CH_2)_5CH_3$	6	28	100	12	6	-	12	-	-	-	82[e]

[a] The reaction was conducted in CH_2Cl_2 under argon at ambient temperature. The starting concentration of each reactant is 0.5 M, $[Pt(acac)_2]=5\times10^{-4}$ M. Irradiation was carried out in 350 nm Rayonet reactor (bandwidth about 40 nm), cooled with a Pyrex jacketed beaker.

[b] After which reactions became very slow.

[c] Determined by GC, decane was used as internal standard.

[d] Identified by GC/MS, relative amounts were determined by GC.

[e] Mixture of internal octenes.

In contrast, we find ethoxy groups increase the reactivity so greatly that the hydrosilylation adduct was essentially the exclusive product. On the other hand, this system also showed olefin dependent product formation. The reactivity of vinyltriethoxysilane is close to that of vinyltriethylsilane judging from both conversion and product formation. Lesser amounts of hydrosilane and olefin were converted in the case of styrene, reflecting deactivation by the phenyl substituent. When methyl acrylate was used, telomerization products were observed, revealing the lower reactivity of the olefin to be hydrosilylated. Interestingly, under identical reaction conditions, most of the 1-octene was converted into a mixture of internal octenes, and these are much less reactive to hydrosilylation.[12] It has been shown that double bonds in linear olefins migrate to yield an equilibrium mixture of isomers in the presence of group VIII metal complexes.[13]

Our study provides a complete picture of product dependent formation on the reactivity of either the hydrosilane or olefin, when possibilities for both photoactivated hydrosilylation addition and ring opening polymerization coexist. It shows that the coordination unsaturation of the Pt complex produced by UV irradiation is capable of mediating essentially all kinds of interactions between reactants, or within reactant itself. Similar reactions have been observed under thermal conditions. We believe that mechanistic facets of such reactions with irradiation activation are similar to those reported for thermal conditions. From a synthetic point of view, it is significant that the desired reaction(s) be favored by carefully tuning the reactivity of reactants.

Acknowledgements

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