

Photoactivated Isomerization of Linear Olefins^{†,‡}

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Abstract: The photocatalyzed (350 nm) isomerization of linear olefins catalyzed by platinum(II) bis(acetylacetonato) [Pt(acac)₂] in the presence of silanes was studied. Catalytic activity depends on the silane. Triphenylsilane is the most reactive silane studied, with more than 98% isomerization of the alkene occurring after 20-min irradiation. There is no concomitant hydrosilylation. The mechanism has been investigated and a metal hydride addition–elimination mechanism proposed.

Transition metal complex catalyzed isomerization of alkenes has been studied extensively.^{1,2} Group VIII metals, rhodium chloride for example, are good catalysts causing the migration of double bonds in linear olefins, yielding an equilibrium distribution of isomers.³ In the presence of nucleophilic cocatalysts such as alcohols, 1-hexene underwent isomerization to 2- and 3-hexene in the presence of rhodium chloride. Similar results were obtained using platinum(II) complexes.³ Speier reported that the hydrosilylation of 2-pentene with certain silicon hydrides in the presence of chloroplatinic acid formed the terminal adducts.⁴ Benkeser also found that in the hydrosilylation of cyclic olefins, the recovered cyclic olefin mixture included all possible isomers.⁵ A stepwise migration of the double bond down the alkyl chain by progressive hydrogen shifts via the intermediacy of the platinum atom has been proposed.⁴

We found that in the Pt(acac)₂-catalyzed photoactivated (350 nm) hydrosilylation of alkynes, if the molar ratio of Et₃SiH to terminal alkyne, 1-hexyne, was 1:1, normal hydrosilylation products were formed. However if the ratio of Et₃SiH to 1-hexyne was increased to 2:1, isomerization of the β-trans product results in *trans*-1-(triethylsilyl)-1-hexene. For the reaction of Et₃SiH with internal alkynes, for instance 2-hexyne, at a molar ratio of 2:1, no isomerization of the β-trans product [*trans*-2-(triethylsilyl)-2-hexene] was observed.

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[‡] This paper is dedicated to Prof. Dr. J. W. Neckers, on the occasion of his 100th birthday.

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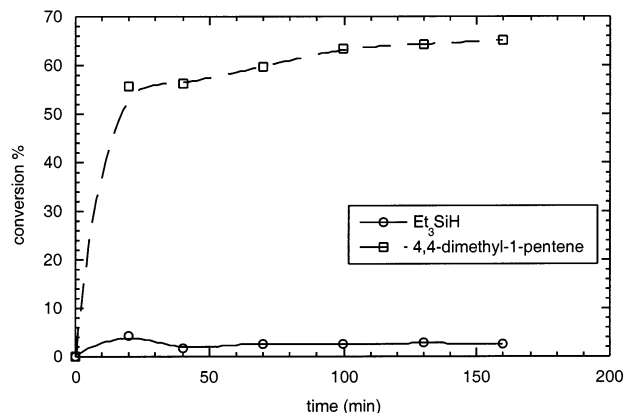


FIGURE 1. Conversion of 4,4-dimethyl-1-pentene to 4,4-dimethyl-2-pentene in the presence of Et₃SiH and Pt(acac)₂. Molar ratio of 4,4-dimethyl-1-pentene:Et₃SiH:Pt(acac)₂ is 1:2:10⁻⁴.

In this paper, we report the photoisomerization (350 nm) in air of linear olefins catalyzed by platinum(II) bis(acetylacetonato) using silanes as the cocatalyst. In control reactions, isomerization was found to also occur without irradiation, but much more slowly. This means that the reaction is a photoactivated isomerization. When only Pt(acac)₂ is used (in the absence of silane), no photoinduced isomerization is observed.

Following 20-min irradiation, a colorless reaction mixture containing 4,4-dimethyl-1-pentene and Et₃SiH turned yellow. After a subsequent period of 2 h in the dark, the isomeric 4,4-dimethyl-2-pentene is obtained with its formation accompanied by formation of a relatively minor amount of hydrosilylation product. Unreacted Et₃SiH remains (Figure 1). The reaction of Et₃SiH with 1-octene under similar conditions gives a mixture of 2-, 3- and 4-octene; however, the reaction rate is much slower than that of Et₃SiH with 4,4-dimethyl-1-pentene.

Ph₃SiH proved to be the most reactive silane. Other cocatalysts investigated were (EtO)₃SiH, Ph₃SiH, ClMe₂SiH, Et₂SiH₂, PhSiH₃, and triisopropylsilane. No hydrosilylation product was formed from the irradiation for 20 min at 350 nm of 4,4-dimethyl-1-pentene (1 part) and Ph₃SiH (2 parts) in the presence of a catalytic quantity of Pt(acac)₂. Decreasing the molar ratio of 4,4-dimethyl-1-pentene to Ph₃SiH to 1:1 also gave complete isomerization after 20-min irradiation (Figure 2).

1-Octene and 1-hexene formed isomers without hydrosilylation immediately after 20-min irradiation in the presence of Ph₃SiH. However, the isomerization of 1-octene or 1-hexene was much slower in the presence of Et₃SiH and took more than 10 h to complete. Hydrosilylation product was formed as well.

Other silanes such as (EtO)₃SiH and ClMe₂SiH formed hydrosilylation adducts but did not catalyze isomerization. With Et₂SiH₂, PhSiH₃, and triisopropylsilane, there were no reaction products. So the number of hydrogen atoms on silicon is not the factor that determines the rate of isomerization. The structure of the alkyl group on the silane is more important. For example, hydride is easy to form from triphenylsilane, because of the stabilization

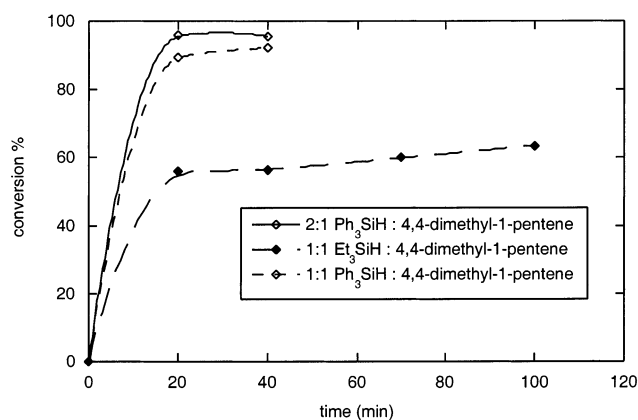


FIGURE 2. Photoisomerization of 4,4-dimethyl-1-pentene in the presence of (a) Ph_3SiH and (b) Et_3SiH . $\text{Pt}(\text{acac})_2$ is the catalyst (molar ratio of 4,4-dimethyl-1-pentene to $\text{Pt}(\text{acac})_2$ is $1:10^{-4}$).

TABLE 1. Conversion of 4,4-Dimethyl-1-pentene in the Presence of Et_3SiH following Irradiation for Different Periods of Time^a

irradiation time (min)	% conversion	
	4,4-dimethyl-1-pentene	Et_3SiH
15	31.61	4.51
25	37.07	6.01
40	61.68	11.09
25 (purged with argon)	97.63	19.54

^a [4,4-Dimethyl-1-pentene] = 1.5 M, [Et_3SiH] = 3.2 M, [$\text{Pt}(\text{acac})_2$] = 1.5×10^{-3} M

of the cation by the three phenyl groups, and this is clearly important.

The conversion of 4,4-dimethyl-1-pentene to 4,4-dimethyl-2-pentene increased, as did the percentage of hydrosilylation product, with increasing irradiation time (Table 1). A reaction mixture purged with argon for 15 min, followed by irradiation for 25 min, led to 98% conversion of 4,4-dimethyl-1-pentene. Both hydrosilylation and isomerization products were observed. The accompanying conversion of Et_3SiH (hydrosilylation product) was approximately 20%. Thus, both increasing the irradiation time and purging the reaction mixture with argon increases the rate of isomerization as well as the percentage of hydrosilylation.

Two mechanisms are proposed in the literature for metal-catalyzed olefin isomerizations. One is the so-called π -allyl mechanism.⁶ The other involves addition–elimination of metal hydride complexes³ (Scheme 1). In our system, we suggest isomerization occurs through the second mechanism. When Et_3SiD was chosen as the hydride source and the $\text{Pt}(\text{acac})_2$ -catalyzed reaction of 4,4-dimethyl-1-pentene was complete, an isotopic ratio of 60:40 was found in the isomer 4,4-dimethyl-2-pentene by GCMS. Since the isotopic ratio found in the isomer 4,4-dimethyl-2-pentene when 4,4-dimethyl-1-pentene is treated with Et_3SiH is 92.7:7.3, a portion of the 4,4-dimethyl-2-pentene is formed containing a deuterated proton. ^1H NMR results were less clear. There was no difference between the spectrum of the product presumed to be

SCHEME 1

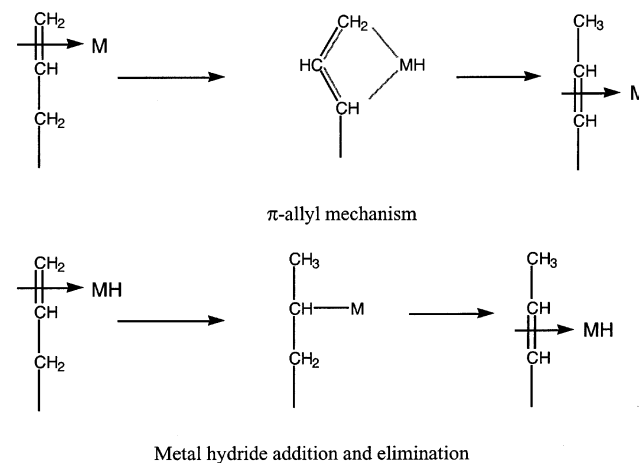


TABLE 2. Integration of the ^1H NMR Spectrum during the Isomerization of 4,4-Dimethyl-1-pentene

time	integration ^a		
	H_a	H_b	H_c
immediately after reaction is complete	2.52	0.54	0.94
2 days after reaction is complete	2.74	0.51	0.74

^a The protons are labeled as H_a for the allylic CH_3 , H_b for the vinyl proton next to CH_3 , and H_c for the other vinyl proton.

D-4,4-dimethyl-2-pentene and 4,4-dimethyl-2-pentene. The multiple peaks assigned to Si–H of Et_3SiD appeared at 3.6 ppm. We suggest that exchange of deuterium in the Et_3SiD with proton likely obtained from 4,4-dimethyl-1-pentene occurred during the isomerization.

The integration of the ^1H NMR spectrum can be used to show the exchange of deuterated proton from Et_3SiD to 4,4-dimethyl-1-pentene. The protons of D-4,4-dimethyl-2-pentene are shown in Table 2. The protons are labeled as H_a for allylic CH_3 , H_b for the vinyl proton next to CH_3 , and H_c for the other vinyl proton. Immediately after the reaction was complete, the deuterium was mainly exchanged with H_b , some with H_a . This is shown mechanistically in Scheme 2. After the reaction mixture was kept in the dark for 2 days, deuterium was distributed over these three positions.

The reaction mechanism is shown in Scheme 3. $(\text{EtO})_3\text{SiH}$ and ClMe_2SiH are the most reactive silanes, while Ph_3SiH is the most unreactive for the hydrosilylation reaction.⁷ For $(\text{EtO})_3\text{SiH}$ and ClMe_2SiH , $k_1 > k_2$, so hydrosilylation occurred. For Ph_3SiH , $k_2 > k_1$, so the hydrogen migration step is much faster than addition of silane to alkene and the main products result from the isomerization reaction.

In summary, the isomerization of linear alkenes catalyzed by $\text{Pt}(\text{acac})_2$ with silane as the cocatalyst at 350-nm irradiation was studied. The competition of the hydrosilylation reaction with isomerization of alkenes is dictated by the choice of silane.

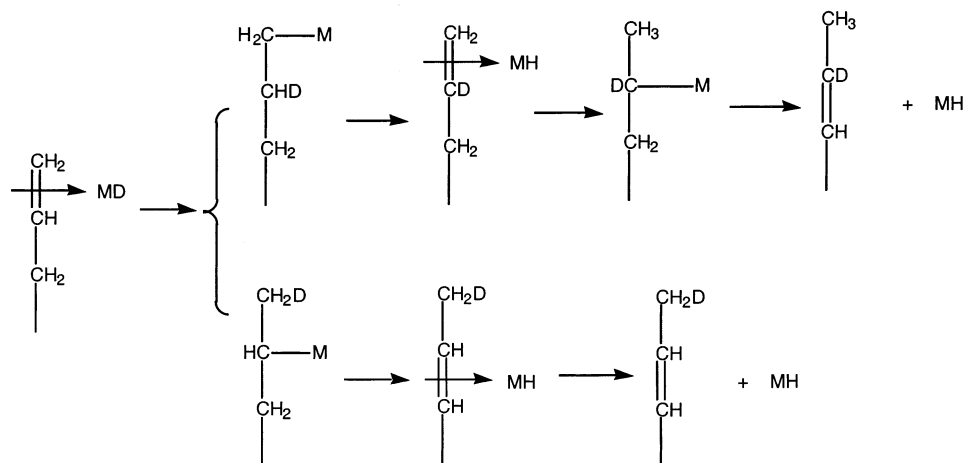
Experimental Section

All commercial chemicals were used as received. Irradiations were carried out in solution in a borosilicate glass container in a Rayonet PRP-100 photochemical reactor equipped with a

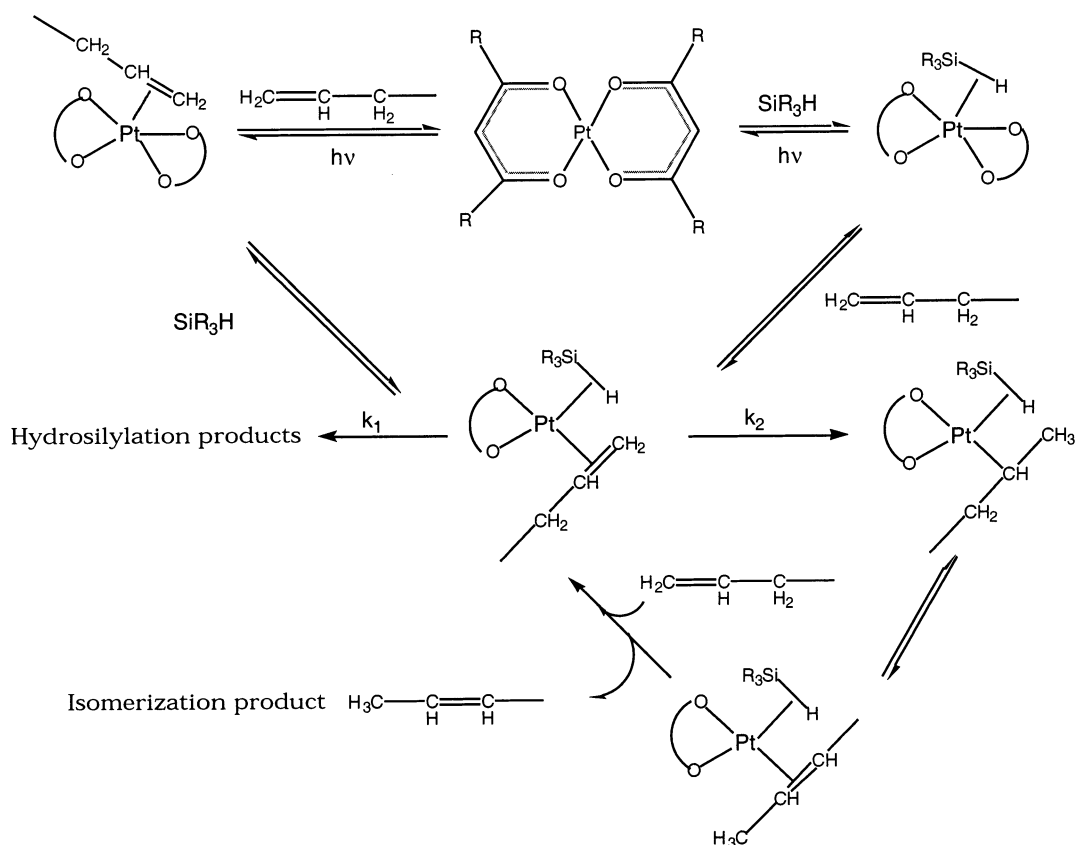
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SCHEME 2



SCHEME 3. Proposed Mechanism for Competition of Isomerization of Olefin with Hydrosilylation



jacketed beaker (Pyrex). 8W×16 RPR-3500 Å lamps from Southern NE Ultraviolet Co. were used. ¹H NMR spectra were recorded in CDCl₃ solution at 200 MHz. Chemical shift values are expressed in ppm relative to tetramethylsilane.

Typically, a mixture of 4,4-dimethyl-1-pentene (0.2 mL, 1.4 mmol) and Et₃SiH (0.44 mL, 2.8 mmol) with Pt(acac)₂ (0.6 mg, 0.07 mmol) contained in a 4-mL vial was irradiated at 350 nm in the photochemical reactor (light intensity, *I*₀, around 10⁻⁸ einstein/s) for 20 min. After the initial irradiation, the reaction

mixture was kept in the dark. GC was used to monitor the reaction and octane was used as internal standard.

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