

Photo-Induced Chromiumcarbonyl Catalyzed Hydrosilylation of Conjugated Dienes with Triethylsilane: The Solvent Effect

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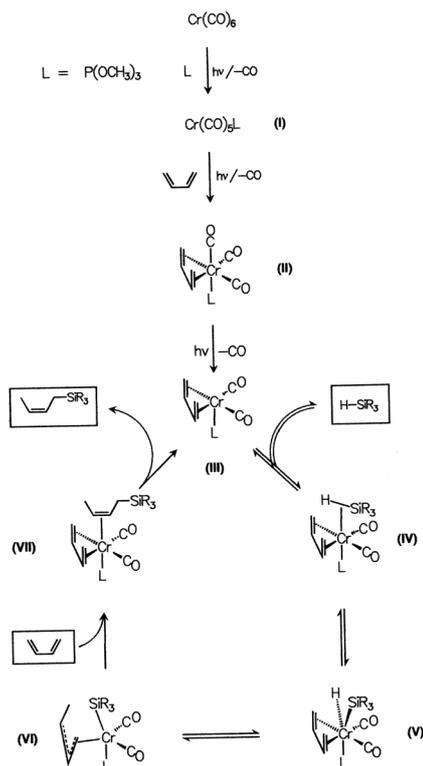
Photocatalytic hydrosilylation of conjugated dienes (1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, *trans*-1,3-pentadiene) with triethylsilane was studied by using $\text{Cr}(\text{CO})_5\text{L}$ ($\text{L} = \text{CO}, \text{P}(\text{CH}_3)_3, \text{P}(\text{OCH}_3)_3, \text{P}(\text{C}_6\text{H}_5)_3, \text{P}(\text{C}_6\text{H}_{11})_3, \text{NC}_5\text{H}_5$) in two very different solvents, toluene and tetrahydrofuran, for comparison with the results found in *n*-hexane. In toluene, the photocatalytic hydrosilylation yields the same products as those in *n*-hexane, with the exception of *trans*-1,3-pentadiene which gives *cis*-1-triethylsilyl-2-pentene as the sole product. However, each of the precursor complexes shows different catalytic activities in toluene and *n*-hexane. The hydrosilylation of 1,3-butadiene in toluene is, in general, significantly faster than that in *n*-hexane. By using $\text{Cr}(\text{CO})_6$, $\text{Cr}(\text{CO})_5[\text{P}(\text{CH}_3)_3]$ or $\text{Cr}(\text{CO})_5[\text{P}(\text{OCH}_3)_3]$ in toluene, the conversion of triethylsilane increases almost linearly as the reaction proceeds, indicating the stability of the active catalyst throughout the reaction, similar to that in *n*-hexane. While no hydrosilylation of 1,3-butadiene could be achieved with $\text{Cr}(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3]$ or $\text{Cr}(\text{CO})_5(\text{NC}_5\text{H}_5)$ in *n*-hexane, the same precursor complexes appear to be active in toluene, though the conversion occurs at much lower rate compared to that obtained using $\text{Cr}(\text{CO})_5[\text{P}(\text{CH}_3)_3]$ or $\text{Cr}(\text{CO})_5[\text{P}(\text{OCH}_3)_3]$. The precursor complex $\text{Cr}(\text{CO})_5[\text{P}(\text{C}_6\text{H}_{11})_3]$ shows catalytic activity neither in toluene nor in *n*-hexane. No photocatalytic hydrosilylation of 1,3-butadiene with triethylsilane was observed in tetrahydrofuran by using any of the precursor complexes. The relative reactivity of conjugated dienes in the hydrosilylation was investigated by using triethylsilane in the presence of $\text{Cr}(\text{CO})_5[\text{P}(\text{OCH}_3)_3]$ as catalyst in toluene, and the same reactivity order was obtained as in *n*-hexane solution: 1,3-butadiene > 3-methyl-1,3-butadiene > 2,3-dimethyl-1,3-butadiene > *trans*-1,3-pentadiene. For all of the dienes, one obtains higher conversion to hydrosilylated product in toluene than in *n*-hexane.

Key words: Photocatalysis, Hydrosilylation, Conjugated Diene, Chromiumcarbonyl

Introduction

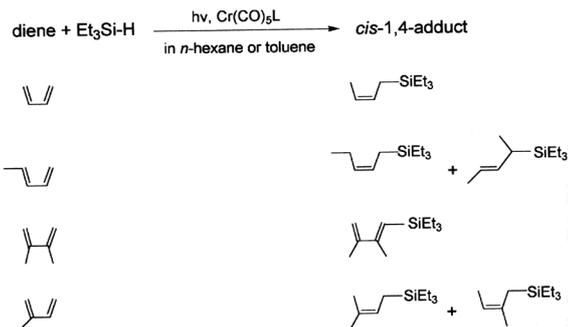
Transition metal complexes have been used extensively as catalysts in the last decades [1]. Platinum, rhodium, nickel, and cobalt complexes have been known to catalyze the addition of a silane $\text{R}_3\text{Si}-\text{H}$ across the $\text{C}=\text{C}$ double bond of monoalkenes [2], while the hydrosilylation of 1,3-dienes are catalyzed by Group 6 metal carbonyls [3]. The hydrosilylation of various conjugated dienes catalyzed by transition metal complexes provides a convenient route to unsaturated organosilicon reagents and serves also as a unique and effective method for the selective formation of carbon-silicon bonds. A typical example is the photocatalytic hydrosilylation of conjugated dienes with triethylsilane using hexacarbonylchromium(0) and hexacarbonylmolybdenum(0) [4]. The chromiumcarbonyl catalyzed hydrosilylation of conjugated dienes yields exclusively the 1,4-adducts. Further-

more, some monosubstituted chromium carbonyl complexes have also been found to catalyze the hydrosilylation of conjugated dienes with triethylsilane in hexane [5]. The latter study has shown that a facial tricarbonyl(trialkylphosphine)(η^4 -1,3-diene)-chromium(0) complex [6] is formed from the photochemical reaction of the diene and the pentacarbonyltrialkylphosphinechromium(0) complex and undergoes a photolytic CO detachment to generate a vacant site available for binding the silane (Scheme 1). Thus, the chromium(0) complex enters the catalytic cycle. Next, the silane coordinates to the vacant site and dissociates into a hydrido and a R_3Si ligands, which are subsequently transferred to the diene. The last step involves the release of the trialkylsilyl product and take-up of a new diene substrate molecule regenerating the active catalyst and completing the catalytic cycle.



Scheme 1. The proposed mechanism for the photocatalytic hydrosilylation of conjugated dienes with triethylsilane in the presence of precursor complexes $\text{Cr}(\text{CO})_5\text{L}$ ($\text{L} = \text{CO}$, $\text{P}(\text{CH}_3)_3$, $\text{P}(\text{OCH}_3)_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$, NC_5H_5).

Photocatalytic hydrosilylation of conjugated dienes by using $\text{Cr}(\text{CO})_5\text{L}$ in *n*-hexane has shown that introduction of trimethylphosphine and trimethylphosphite, $\text{L} = \text{P}(\text{CH}_3)_3$ and $\text{P}(\text{OCH}_3)_3$, increases the catalytic activity remarkably compared to that of $\text{Cr}(\text{CO})_6$, while the $\text{Cr}(\text{CO})_5\text{L}$ complexes with $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$, NC_5H_5 have been found to be catalytically inactive. The catalytic inactivity of $\text{Cr}(\text{CO})_5[\text{P}(\text{C}_6\text{H}_{11})_3]$ is due to the steric crowding of the ligand hindering the coordination of the diene to the chromium. The reason for the inactivity of $\text{Cr}(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3]$ and $\text{Cr}(\text{CO})_5[(\text{NC}_5\text{H}_5)]$ may be their low solubility in *n*-hexane. Therefore, we decided to study the solvent effects in the hydrosilylation of conjugated dienes by using $\text{Cr}(\text{CO})_5\text{L}$ complexes as catalysts. Here, we report the results of such a comprehensive study on the hydrosilylation of 1,3-butadiene, 2-methyl-1,3-butadiene, *trans*-1,3-pentadiene, and 2,3-dimethyl-1,3-butadiene with triorganosilanes (alkyl = C_2H_5 , C_6H_5) in the presence of $\text{Cr}(\text{CO})_5\text{L}$



Scheme 2. Photocatalytic hydrosilylation of 1,3-dienes with triethylsilane in the presence of $\text{Cr}(\text{CO})_5\text{L}$ ($\text{L} = \text{CO}$, $\text{P}(\text{CH}_3)_3$, $\text{P}(\text{OCH}_3)_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, NC_5H_5) in *n*-hexane or toluene. All the precursor complexes are found to be active in toluene, while only $\text{Cr}(\text{CO})_6$, $\text{Cr}(\text{CO})_5\text{P}(\text{CH}_3)_3$, and $\text{Cr}(\text{CO})_5\text{P}(\text{OCH}_3)_3$ are active in *n*-hexane. In the case of 1,3-*trans*-pentadiene, the 1,2-hydrosilylation product (*trans*-4-triethylsilyl-2-pentene) is obtained as minor product only in *n*-hexane.

($\text{L} = \text{CO}$, $\text{P}(\text{CH}_3)_3$, $\text{P}(\text{OCH}_3)_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$, NC_5H_5) using *n*-hexane, toluene, and tetrahydrofuran as solvent.

Experimental Section

All reactions and manipulations involving the metal carbonyl catalysts were carried out either in a vacuum or under dry inert atmosphere (N_2 , Ar). Photochemical reactions were carried out in an immersion-well apparatus (solidex glass, $\lambda > 280$ nm) by using a Hanau TQ 150 or a Philips HPK 125-W high pressure mercury lamp, which was cooled by circulating water or precooled methanol.

Solvents were distilled after refluxing over metallic sodium or phosphorus pentoxide under nitrogen for several days. Triorganosilanes ($\text{R} = \text{C}_6\text{H}_5$, C_2H_5) (Merck) and hexacarbonylchromium(0) (Aldrich) were commercially available and used without further purification. The dienes (except 1,3-butadiene) were commercially available (Fluka) and distilled before used. $\text{Cr}(\text{CO})_5\text{L}$ ($\text{L} = \text{P}(\text{CH}_3)_3$, $\text{P}(\text{OCH}_3)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{C}_5\text{H}_5\text{N}$) were prepared according to the literature procedures starting from $\text{Cr}(\text{CO})_5\text{THF}$ [7].

All of the hydrosilylation products obtained in toluene were found to have the same spectroscopic data as reported in literature [4] except *trans*-1,3-pentadiene. In the case of *trans*-1,3-pentadiene, only one isomer was obtained, *cis*-1-triethylsilyl-2-pentene. The progress of the hydrosilylation reactions was monitored by observing the disappearance of the characteristic Si-H absorption band at around 2120–2100 cm^{-1} in the IR spectrum together with changes in the CO region.

NMR spectra were recorded on a Bruker AC-80 spectrometer (80.131 MHz for ^1H , 20.149 MHz for ^{13}C), and

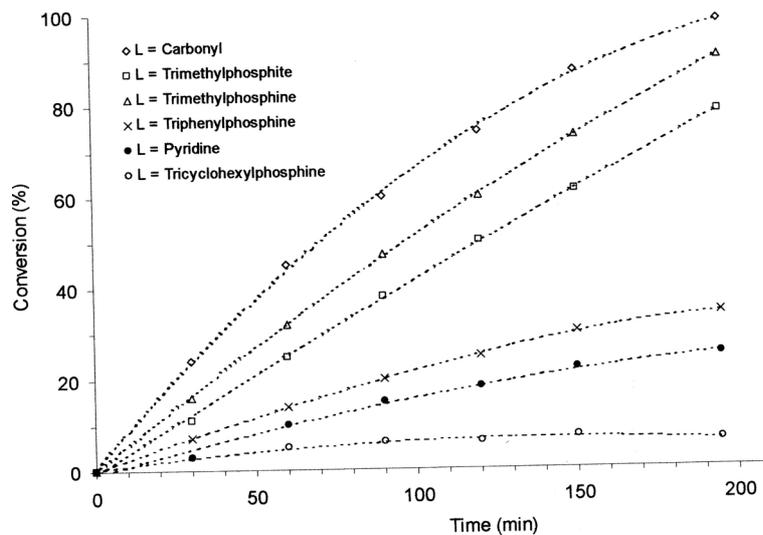


Fig. 1. Conversion of triethylsilane *versus* time plots for the photocatalytic hydrosilylation of 1,3-butadiene by using six different precursor complexes $\text{Cr}(\text{CO})_5\text{L}$ in toluene at room temperature (molar ratio of triethylsilane : diene: complex is 10:20:1).

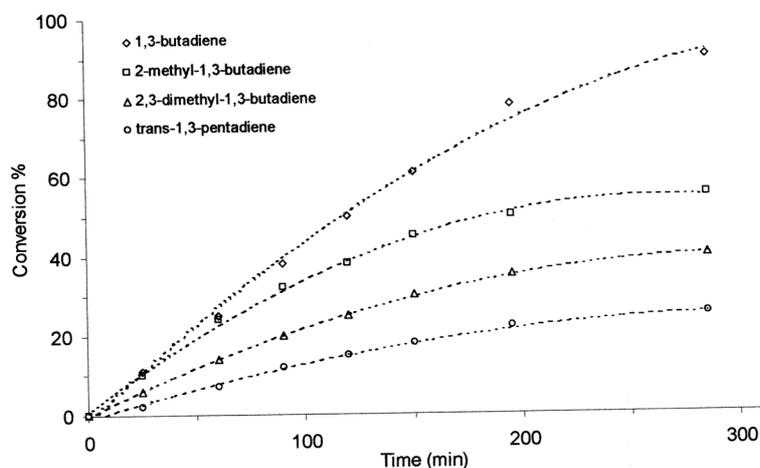


Fig. 2. Conversion *versus* time plots for different conjugated dienes in the photocatalytic hydrosilylation with triethylsilane using $\text{Cr}(\text{CO})_5[\text{P}(\text{OCH}_3)_3]$ as precursor in toluene solution at room temperature (molar ratio of triethylsilane: diene: complex is 10:20:1).

a Bruker AM 400 spectrometer (400.1 MHz for ^1H , 100.6 MHz for ^{13}C) using TMS as internal reference. A Nicolet FT-IR spectrophotometer was used to follow the changes in the $\nu_{\text{Si-H}}$ and ν_{CO} spectral regions in monitoring the reactions. Routine gas chromatographic analyses were performed on a Perkin Elmer F33 chromatograph using a flame ionization detector and a 6 ft OV-1 column or a Varian 3700 instrument.

Results and Discussion

As in the previous work on the photocatalytic hydrosilylation of dienes by using $\text{Cr}(\text{CO})_5\text{L}$ in *n*-hexane [5], the same catalytic reaction was also tested on the dienes (1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, *trans*-1,3-pentadiene) with tri-

ethylsilane in two more different solvents, toluene and tetrahydrofuran. In toluene, the photocatalytic hydrosilylation was found to yield the same products as that in *n*-hexane, with the exception of *trans*-1,3-pentadiene which gives only one hydrosilylation product (*cis*-1-triethylsilyl-2-pentene). Scheme 2 summarizes the photocatalytic hydrosilylation in *n*-hexane and toluene in terms of reaction products. Since the same products are essentially obtained in both solvents, the mechanism given in Scheme 1 can also be adopted for the hydrosilylation of dienes with triethylsilane in toluene.

Although the hydrosilylation gives essentially the same products in *n*-hexane and toluene, the catalytic activities of the same precursor complex in two solvents appears to differ from each other. The plot for

the percent conversion of triethylsilane *versus* time (Fig. 1) reflects the relative activities of the precursor complexes $\text{Cr}(\text{CO})_5\text{L}$ ($\text{L} = \text{CO}, \text{P}(\text{CH}_3)_3, \text{P}(\text{OCH}_3)_3, \text{P}(\text{C}_6\text{H}_{11})_3, \text{P}(\text{C}_6\text{H}_5)_3, \text{C}_5\text{H}_5\text{N}$) for the hydrosilylation of 1,3-butadiene with triethylsilane in toluene. In the case of $\text{Cr}(\text{CO})_6$, the hydrosilylation is quite fast at the beginning of the reaction. However, the rate of conversion decreases as the reaction proceeds. This trend is similar to that observed for the hydrosilylation of 1,3-butadiene by using $\text{Cr}(\text{CO})_6$ in *n*-hexane (Fig. 2, elsewhere [5]). The reaction in toluene is significantly faster than that in *n*-hexane. In the case of $\text{Cr}(\text{CO})_5[\text{P}(\text{CH}_3)_3]$ and $\text{Cr}(\text{CO})_5[\text{P}(\text{OCH}_3)_3]$, the conversion of triethylsilane increases almost linearly as the reaction proceeds, indicating the stability of the active catalyst throughout the reaction. This has also been observed in *n*-hexane. Photocatalytic hydrosilylation of 1,3-butadiene is found to be faster in toluene by using $\text{Cr}(\text{CO})_5[\text{P}(\text{CH}_3)_3]$ or $\text{Cr}(\text{CO})_5[\text{P}(\text{OCH}_3)_3]$ than that in *n*-hexane (the conversion attained after 200 min irradiation in toluene is 75% or 85%, respectively, while 55% or 65% conversion is obtained at the same irradiation time in *n*-hexane under the same experimental conditions).

In the case of the complexes $\text{Cr}(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3]$ and $\text{Cr}(\text{CO})_5[\text{NC}_5\text{H}_5]$, the hydrosilylation of 1,3-butadiene with triethylsilane occurs with much lower rate compared to $\text{Cr}(\text{CO})_5[\text{P}(\text{CH}_3)_3]$ and $\text{Cr}(\text{CO})_5[\text{P}(\text{OCH}_3)_3]$ in toluene (Fig. 1). On the other hand, with these two complexes no hydrosilylation of 1,3-butadiene could be achieved in *n*-hexane [5], because of their insolubility. Since they are quite soluble in toluene, they form active catalyst upon irradiation. However, one obtains much lower conversions for the hydrosilylation of 1,3-butadiene by using these two complexes than in toluene (Fig. 1). The conversion attained for the hydrosilylation of 1,3-butadiene with triethylsilane by using $\text{Cr}(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3]$ and $\text{Cr}(\text{CO})_5[\text{NC}_5\text{H}_5]$ after 200 min irradiation in toluene is 32% or 26%, respectively, while 85% or 75% conversion is obtained at the same irradiation time in toluene under the same experimental conditions. The lower catalytic activity of $\text{Cr}(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3]$ and $\text{Cr}(\text{CO})_5[\text{NC}_5\text{H}_5]$ compared to $\text{Cr}(\text{CO})_5[\text{P}(\text{CH}_3)_3]$ and $\text{Cr}(\text{CO})_5[\text{P}(\text{OCH}_3)_3]$ for hydrosilylation is attributed to the lower π -acceptor ability of triphenylphosphine and pyridine compared to trimethylphosphine or trimethylphosphite [8], causing the Cr—CO bonds to be stronger in $\text{Cr}(\text{CO})_5\text{L}$ and thus less susceptible to

the CO substitution with substrates forming the active catalyst (Scheme 1).

$\text{Cr}(\text{CO})_5[\text{P}(\text{C}_6\text{H}_{11})_3]$ does neither show any catalytic activity in toluene, nor in the hydrosilylation of 1,3-butadiene with triethylsilane in *n*-hexane. Since $\text{Cr}(\text{CO})_5[\text{P}(\text{C}_6\text{H}_{11})_3]$ is quite soluble in *n*-hexane and in toluene [9] it is conceivably that the catalytic inactivity is due to the bulky tricyclohexylphosphine ligand (the cone angle is 170° [10]), which hinders the coordination of substrates to the chromium forming the active catalyst.

When a solution of 1,3-butadiene and triethylsilane is irradiated in tetrahydrofuran in the presence of $\text{Cr}(\text{CO})_6$ at room temperature, no hydrosilylation of the diene was observed. The only observable reaction is the gradual substitution of CO in $\text{Cr}(\text{CO})_6$ by tetrahydrofuran. Obviously, tetrahydrofuran as a coordinating solvent does not allow the substrate coordination since it is in large excess compared to the substrate concentrations (about 200:1 ratio).

The relative reactivity of conjugated dienes in the hydrosilylation was investigated by using triethylsilane in the presence of $\text{Cr}(\text{CO})_5[\text{P}(\text{OCH}_3)_3]$ as catalyst in toluene. Figure 2 shows the conversion *versus* time plots for different conjugated dienes in the photocatalytic hydrosilylation with triethylsilane using $\text{Cr}(\text{CO})_5[\text{P}(\text{OCH}_3)_3]$ as precursor in toluene solution at room temperature. It was found that the conversion of triethylsilane decreases in the same order as that observed in *n*-hexane solution [5]: 1,3-butadiene > 3-methyl-1,3-butadiene > 2,3-dimethyl-1,3-butadiene > *trans*-1,3-pentadiene. This could be due to steric hindrance between the methyl group(s) of the diene and the trimethylphosphite ligand on the catalytically active species. Another point that deserves attention is that the conversion of triethylsilane is more complete for all the dienes in toluene than that in *n*-hexane. This clearly shows that toluene is a better solvent for the photocatalytic hydrosilylation of conjugated dienes with triethylsilane.

The photocatalytic 1,4-addition of triphenylsilane, $\text{HSi}(\text{C}_6\text{H}_5)_3$, to conjugated dienes in the presence of $\text{Cr}(\text{CO})_5\text{L}$ ($\text{L} = \text{CO}, \text{P}(\text{CH}_3)_3, \text{P}(\text{OCH}_3)_3, \text{P}(\text{C}_6\text{H}_5)_3, \text{P}(\text{C}_6\text{H}_{11})_3, \text{C}_5\text{H}_5\text{N}$) could not be achieved during the irradiation in toluene. This may be due to the steric and/or electronic effects arising from the presence of the phenyl groups, which prevent the coordination of the silane to the chromium.

The overall results obtained from this research show first of all that toluene is a better solvent than *n*-hexane for the photocatalytic hydrosilylation of conjugated dienes in the presence of Cr(CO)₅L (L = CO, P(CH₃)₃, P(OCH₃)₃, P(C₆H₅)₃, C₅H₅N). As mentioned before, this could be explained by the higher solubility of catalytic species in toluene than in *n*-hexane. Secondly, the reactivity order of conjugated dienes is found to be the same in *n*-hexane and toluene but for all of the conjugated dienes, the conversion of triethylsilane increases considerably on changing the solvent from *n*-hexane to toluene. On the other hand, no hydrosilylation product was obtained in tetrahydrofuran,

which clearly indicates that this solvent is not suitable for the photocatalytic hydrosilylation of conjugated dienes with trialkylsilane. This may be due to the fact that tetrahydrofuran is a coordinating ligand, which prevents the coordination of substrates to the chromium center, particularly when used in large excess as solvent.

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