

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

Ceyhan Kayran, Saim Özkar, and Vagif M. Akhmedov

Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

Reprint requests to Assoc. Prof. Dr. C. Kayran. E-mail: ckayran@metu.edu.tr

Z. Naturforsch. **58b**, 644 – 648 (2003); received March 31, 2003

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