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# Completely selective synthesis of (*E*)-β-(triethylsilyl)styrenes by $Fe_3(CO)_{12}$-catalyzed reaction of styrenes with triethylsilane

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## Abstract

Using $Fe_3(CO)_{12}$ as the catalyst, the reaction of styrenes ($C_6H_5CH{=}CH_2$, *p*-$CH_3C_6H_4CH{=}CH_2$, *p*-$ClC_6H_4CH{=}CH_2$, and *p*-$CH_3OC_6H_4CH{=}CH_2$) with triethylsilane gave (*E*)-β-(triethylsilyl)styrenes (**2a**, (*E*)-$C_6H_5CH{=}CHSiEt_3$; **2b**, (*E*)-*p*-$CH_3C_6H_4CH{=}CHSiEt_3$; **2c**, (*E*)-*p*-$ClC_6H_4CH{=}CHSiEt_3$; **2d**, (*E*)-*p*-$CH_3OC_6H_4CH{=}CHSiEt_3$) in 66–89% yields with complete selectivity. Similarly, $Fe_2(CO)_9$ also catalyzed dehydrogenative silylation again, with complete selectivity but in low yields. The reaction of styrene with treithylsilane, catalyzed by $Os_3(CO)_{12}$, gave a mixture of the corresponding vinylsilane (dehydrogenative silylation product) and alkylsilane (hydrosilylation product).

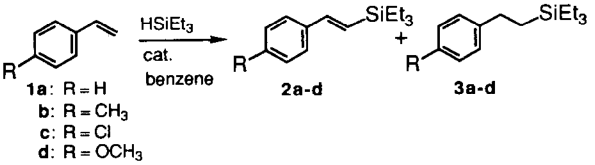
## 1. Introduction

Catalytic addition of hydrosilanes to alkenes, hydrosilylation, in the presence of a wide variety of transition metal complexes is well established [1]. It has been noted that sometimes these reactions are accompanied by the formation of vinylsilanes [2,3]. To the best of our knowledge, the first example of the highly selective formation of vinylsilanes is the $Fe(CO)_5$-catalyzed reaction of ethylene with $HSiEt_3$ reported by Nesmeyanov in 1962 [4]. Since then, no example of the exclusive formation of vinylsilanes was reported until we found the $Ru_3(CO)_{12}$-catalyzed reaction of styrenes with $HSiEt_3$ in 1980 [5]. The number of examples of highly selective dehydrogenative silylation is still limited [6–8].

We report here the results of examination of the catalytic activities of $M_3(CO)_{12}$ (M = Fe, Ru, Os) for dehydrogenative silylation of styrenes with a hydrosilane. Among these catalysts, $Fe_3(CO)_{12}$ exhibited complete selectivity.

## 2. Results and discussion

Our previous observations on $Ru_3(CO)_{12}$ catalyst [5,6] led us to examine the effectiveness of iron-triad carbonyl complexes, $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $Os_3(CO)_{12}$, as the catalyst for the reaction of styrene with triethylsilane (eqn. (1)).



(1)

The results are listed in Table 1. Iron- and osmium-carbonyl complexes other than $Fe(CO)_5$ also showed the same catalytic activities for the reaction of styrene with $HSiEt_3$ as $Ru_3(CO)_{12}$. The results were similar to those obtained for $Ru_3(CO)_{12}$ with respect to the formation of β-silylstyrene and of almost the same amount of ethylbenzene (not shown in Table 1). It is noteworthy that $Fe_3(CO)_{12}$ is the catalyst that exhibited the highest, most complete selectivity. In the case of the $Fe_3(CO)_{12}$-catalyzed reaction, lower reaction temperatures gave better yields of **2a** but a longer reaction time was required (runs 3–5). On the other hand, the $Os_3(CO)_{12}$-catalyzed reaction afforded a mixture of **2a** and **3a** whose ratio depended on the reaction temperature (runs 9–11).

The results of the $Fe_3(CO)_{12}$- and $Os_3(CO)_{12}$-catalyzed reaction of *p*-substituted styrenes with triethylsilane are summarized in Table 2. The use of $Fe_3(CO)_{12}$ gave only (*E*)-β-triethylsilylstyrenes (**2b–d**) in 66–70%

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TABLE 1. Reaction of styrene **1a** with triethylsilane in the presence of iron-triad carbonyl complexes [a]

| Run | Catalyst | Temp. (°C) | Time (h) | Yield [b] (%) | |
|---|---|---|---|---|---|
| | | | | **2a** | **3a** |
| 1 | $Fe(CO)_5$ | 60 | 24 | 0 | 0 |
| 2 | $Fe_2(CO)_9$ | 60 | 24 | 36 | 0 |
| 3 [c] | $Fe_3(CO)_{12}$ | 40 | 72 | 89 | 0 |
| 4 [c] | | 60 | 24 | 81 (74) [d] | 0 |
| 5 [c] | | 80 | 24 | 71 | 0 |
| 6 | $Ru_3(CO)_{12}$ | 40 | 110 | 84 | trace |
| 7 | | 60 | 15 | 92 | trace |
| 8 | | 80 | 5 | 93 | 0.2 |
| 9 | $Os_3(CO)_{12}$ | 40 | 72 | 24 | 12 |
| 10 | | 60 | 24 | 84 | 7 |
| 11 | | 80 | 6 | 92 | 3 |

[a] Reaction conditions: triethylsilane (5 mmol), styrene (15 mmol), catalyst (0.05 mmol), benzene (5 ml). [b] Yields were determined by GLC using tetradecane as an internal standard and were based on triethylsilane. [c] Reaction was run in the presence of 0.1 mmol of $Fe_3(CO)_{12}$. [d] Isolated yield.

GLC yields. A longer reaction time (48 h) was necessary for the reaction of *p*-methyl- and *p*-chlorostyrenes to achieve high yields. When the reactions were performed in the presence of $Os_3(CO)_{12}$, the mixture of vinyl- and alkylsilanes was obtained. In the case of $Ru_3(CO)_{12}$-catalyzed reaction of *p*-substituted styrenes (**1b–d**) with triethylsilane, the hydrosilylation products **3b**, **3c**, and **3d** were obtained in 1, 0.5, and 0.3% GLC yields, respectively.

The reaction of 1-hexene with treithylsilane in the presence of $Fe_3(CO)_{12}$ afforded a complex mixture including vinylsilane (6%), allylsilane (17%), and alkylsilane (7%) [6]. $Fe_3(CO)_{12}$ is not effective for the reaction with acrylonitrile and methylacrylate.

The discovery that $Fe_3(CO)_{12}$ can effect completely selective dehydrogenate silylation of styrenes with a hydrosilane may be synthetically important since separation of simple addition products from dehydrogenative silylation products is generally difficult. The search for other catalyst systems which would enable the conversion of other alkenes to vinylsilanes is now in progress.

TABLE 2. Reaction of *p*-substituted styrenes with triethylsilane [a]

| Run | Substrate | Catalyst [b] | Temp. (°C) | Time (h) | Yield [c] (%) | |
|---|---|---|---|---|---|---|
| | | | | | **2** | **3** |
| 1 | **1b** | $Fe_3(CO)_{12}$ | 60 | 48 | 67 | 0 |
| 2 | **1b** | $Os_3(CO)_{12}$ | 80 | 6 | 94 | 3 |
| 3 | **1c** | $Fe_3(CO)_{12}$ | 60 | 48 | 66 | 0 |
| 4 | **1c** | $Os_3(CO)_{12}$ | 80 | 6 | 96 | 4 |
| 5 | **1d** | $Fe_3(CO)_{12}$ | 60 | 24 | 70 | 0 |
| 6 | **1d** | $Os_3(CO)_{12}$ | 80 | 6 | 88 | 6 |

[a] Reaction conditions: triethylsilane (5 mmol), substrate (15 mmol), benzene (5 ml). [b] $Fe_3(CO)_{12}$ (0.1 mmol) and $Os_3(CO)_{12}$ (0.025 mmol) were used. [c] Yields were determined by GLC using tetradecane as an internal standard and were based on triethylsilane.

## 3. Experimental section

During the reaction, all manipulations were carried out under nitrogen. The products were determined by comparison with NMR and IR data of authentic samples. Benzene was dried over $CaH_2$, hexane over sodium and both were distilled under nitrogen. Styrenes and triethylsilane were commercially available and were purified by distillation. $Fe(CO)_5$, $Fe_2(CO)_9$, and $Os_3(CO)_{12}$ were commercially available and used without further purification. $Fe_3(CO)_{12}$ was obtained from Strem Chemicals, Inc., Newburyport, MA. When $Fe_3(CO)_{12}$ was used without further purification (commercial grade), the reproducibility of the reaction was poor. To avoid this difficulty purification of $Fe_3(CO)_{12}$ was carried out in the following way [9]. $Fe_3(CO)_{12}$(4–5 g) was placed in a thimble of a Soxhlet apparatus. Metallic impurities were removed by means of continuous extraction with hot hexane (200 ml) under nitrogen for 12 h. The extract was evaporated under vacuum at room temperature to give dark green solids (3–3.5 g), which were used without further purification.

### *3.1. Preparation of (E)-β-(triethylsilyl)styrenes **2a–d***

The following procedure for (*E*)-1-phenyl-2-(triethylsilyl)ethylene (**2a**) is typical. A 10 ml two-necked flask equipped with a reflux condenser, a rubber septum cap, and a magnetic stirring bar was dried with free flame three times by vacuum-nitrogen flow cycles and then nitrogen was charged in the flask. In the flask was placed $Fe_3(CO)_{12}$ (50 mg, 0.1 mmol), purified in a manner described above, and these solids were then dissolved in 5 ml of benzene. To this resulting solution were added triethylsilane (580 mg, 5 mmol), styrene (1620 mg, 15 mmol), and tetradecane (322 mg). The flask was carefully evacuated using a 5 mmHg vacuum line at room temperature until the solution just began to boil, and then the flask was rapidly refilled with nitrogen at atmospheric pressure. This procedure was repeated three times. The solution was heated at 60°C for 24 h with stirring. Analysis of the reaction mixture by GLC (tetradecane as an internal standard) showed **2a** and ethylbenzene in 81 and 80% yields, respectively. Kugelrohr distillation of the reaction mixture (100°C/10 mmHg) afforded the analytically pure sample. (*E*)-1-Phenyl-2-(triethylsilyl)ethylene (**2a**), (*E*)-1-(*p*-methylphenyl)-2-(triethylsilyl)ethylene (**2b**), (*E*)-1-(*p*-chlorophenyl)-2-(triethylsilyl)ethylene (**2c**), and (*E*)-1-(*p*-methoxyphenyl)-2-(triethylsilyl)ethylene (**2d**) have been previously characterized [6].

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