

Rhodium-Catalyzed Insertion of Carbenoids into β C–H Bonds of Silacycloalkanes: A Facile and General Approach to Functionalized Silacycloalkanes

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Silacycloalkanes are useful building blocks as starting materials for the stereo- and regioselective synthesis of alcohols and alkenes¹ and as monomers for the synthesis of organosilicon polymers.² In addition, those compounds have also attracted attention as synthetic drugs and agrochemicals because of their specific and high biological activity.³ Although functionalized silacycloalkanes would be potentially useful precursors of highly functionalized organic compounds, straightforward methods for introducing a functional group into silacycloalkanes have not been realized yet. Several efforts have been made to introduce halogen or ester functionalities into silacycloalkanes by insertion reactions of dichlorocarbene⁴ or (alkoxycarbonyl)carbenes,⁵ however, these methods have suffered from low selectivity of the reactions and/or low reactivity of carbenes. We report herein the first successful examples of regioselective introduction of an ester functionality into the β position of silacycloalkanes by means of the $\text{Rh}_2(\text{OAc})_4$ -catalyzed C–H insertion reactions of α -diazo esters (Scheme 1).⁶

The following procedure for the preparation of 3-[(*tert*-butoxycarbonyl)methyl]-1,1-dimethyl-1-silacyclobutane (**2a (Bu)**) is representative (Table 1). To a solution of 37 mg (0.37 mmol) of 1,1-dimethyl-1-silacyclobutane (**1a**) and 4.1 mg (0.009 mmol) of $[(\text{CH}_3\text{COO})_2\text{Rh}]_2$ in 0.5 mL of dichloromethane was added 158 mg (1.11 mmol) of *tert*-butyl diazoacetate over a period of 4 h by using a syringe pump

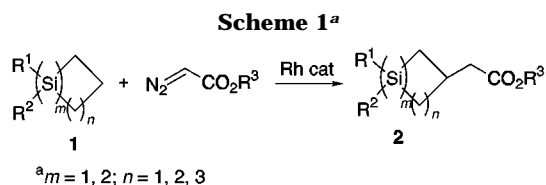


Table 1. Rh-Catalyzed Insertion of α -Diazo Esters into Silacycloalkanes^{a†}

| silacycloalkane | diazo ester | reaction time/h | Product (% yield) ^b |
|-----------------|--|-----------------|----------------------------------|
| | $\text{N}_2=\text{CH}-\text{CO}_2\text{tBu}$ | 4 | 2a (Bu) (90) |
| 1a | $\text{N}_2=\text{CH}-\text{CO}_2\text{Et}$ | 4 | 2a (Et) (95) |
| 1a | $\text{N}_2=\text{CH}-\text{CO}_2\text{Et}$ | 4 | 2a (Et) (97) ^c |
| | $\text{N}_2=\text{CH}-\text{CO}_2\text{tBu}$ | 18 | 2b (85) ^d |
| | $\text{N}_2=\text{CH}-\text{CO}_2\text{tBu}$ | 18 | 2c (63) |
| | $\text{N}_2=\text{CH}-\text{CO}_2\text{Et}$ | 4 | 2d (91) |
| | $\text{N}_2=\text{CH}-\text{CO}_2\text{Et}$ | 2 | 2e (62) |

^a Silacycloalkanes (0.2–0.4 mmol) were reacted with α -diazo esters (1.1–4.0 eq) in the presence of $\text{Rh}_2(\text{OAc})_4$ (2.5 mol%) in dichloromethane (0.5 mL) at room temperature.

^b Isolated yields. ^c Reactions were carried out in 10 mL of dichloromethane with 5 mmol of silacyclobutane, 7.5 mmol of ethyl diazoacetate, and 0.1 mmol of $\text{Rh}_2(\text{OAc})_4$ (2.0 mol%).

^d $\text{Rh}_2(\text{OAc})_4$ (5.0 mol%) was used.

in a nitrogen atmosphere at room temperature. After completion of the addition, the reaction mixture was stirred for another 30 min and then concentrated. The crude product was purified by silica gel column chromatography (ethyl acetate:hexane = 1:18) to give 71.6 mg (0.33 mmol, 90%) of **2b (Bu)** as a colorless liquid.⁷

This reaction seems to be fairly general. Thus, under the similar conditions, carbenoids generated by the catalytic decomposition of the α -diazo esters smoothly inserted into the β C–H bonds of silacyclopentane **1b**, silacyclohexane **1c**, and disilacyclopentanes **1d** and **1e**,⁸ giving the corresponding insertion products **2** in high yields (Table 1). The reactivity of the silacycloalkanes was found to be decisively dependent on the ring structure and the nature of a substituent on the silicon (*vide infra*); thus, **1a** and **1d** exhibited the highest reactivity. When less reactive silacycloalkanes such as **1b** and **1c** were employed as substrates, yields of the insertion products **2b** and **2c** were considerably decreased by competitive dimerization of carbenoids. In such cases, slow addition of the diazo esters to the reaction solution over a period of 18 h was essential for achieving the satisfactory results. As the catalyst, related Rh complexes other than $[(\text{CH}_3\text{COO})_2\text{Rh}]_2$ were less effective. For instances, $[(\text{CF}_3\text{COO})_2\text{Rh}]_2$ and $[(\text{CH}_3(\text{CH}_2)_6\text{COO})_2\text{Rh}]_2$ catalyzed the reaction of *tert*-butyl diazoacetate with **1c** to afford **2c** in lower yields (36% and 20%, respectively).

The extremely high regioselectivity of the present reactions deserves special comments. In most cases, no signifi-

(8) Silacycloalkanes used in this work except for disilacyclopentanes are commercially available. Disilacyclopentanes were prepared by the Na/K-promoted cyclization of 1,3-bis(chlorosilyl)propanes: Kumada, M.; Tamao, K.; Takubo, T.; Ishikawa, M. *J. Organomet. Chem.* **1967**, *9*, 43.

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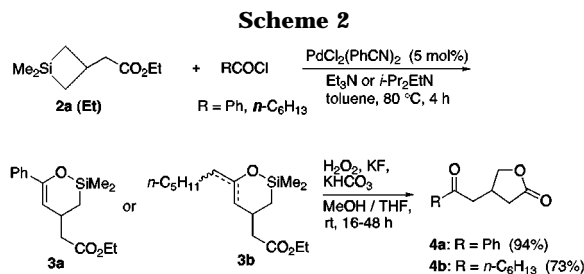
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(7) IR (neat): 2966, 1731, 1369, 1251, 1162, 1096, 806 cm^{-1} . ¹H NMR (300 MHz, C_6D_6) δ : 0.20 (s, 3H), 0.22 (s, 3H), 0.63 (ddd, $J = 12.3, 10.1, 3.0$ Hz, 2H), 1.15 (ddd, $J = 12.3, 8.24, 3.0$ Hz, 2H), 1.38 (s, 9H), 2.24 (d, $J = 7.5$ Hz, 2H), 2.53 (m, 1H). ¹³C NMR-DEPT (75.5 MHz, C_6D_6) δ : -1.7 (CH_3), 1.5 (CH_3), 21.5 (CH_2), 28.4 (CH_3), 29.9 (CH), 47.7 (CH_2), 80.0 (C), 172.5 (CO). ²⁹Si NMR (59.6 MHz, C_6D_6) δ : 7.95. MS (EI, 70 eV) m/z (relative intensity): 199 ($\text{M}^+ - \text{Me}$, 0.2), 158 (4), 141 (12), 116 (92), 99 (48), 75 (84), 57 (100). Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{O}_2\text{Si}$: C, 61.63; H, 10.34. Found: C, 61.82; H, 10.44.



cant side products such as other regioisomers and ring expansion products arising from Si–C bonds insertion of carbenoids were observed. For example, the reactions of α -diazo esters with **1a** cleanly gave **2a** (Bu) or **2a** (Et) as a sole product, whereas dichlorocarbene^{4b} and singlet methylene¹⁰ were known to react with **1a** at both the C–H and the Si–C bonds to afford a mixture of products. Moreover, in contrast to photochemical reactions of α -diazo esters with **1b** in which three regioisomers were formed via insertion of (alkoxycarbonyl)carbenes into the various C–H bonds,⁵ the Rh-catalyzed reaction of the same substrates selectively gave β C–H bond insertion product **2b** in 85% yield with no trace of other isomers. The selective carbenoid insertion into the β C–H bonds of disilacyclopentanes **1d** and **1e** were also efficiently catalyzed by $\text{Rh}_2(\text{OAc})_4$, furnishing the high yields of the corresponding insertion products **2d** and **2e** without Si–Si bond insertion, though the Si–Si bonds of disilacycloalkanes are quite reactive to a variety of insertion reactions.¹⁰

A competition reaction between silacyclohexane **1c** and an acyclic alkylsilane such as hexyltrimethylsilane with the α -diazo ester revealed the superior reactivity of **1c**. Thus, when a 1:2 mixture of **1c** and hexyltrimethylsilane was allowed to react with *tert*-butyl diazoacetate in the presence of 2.5 mol % of $\text{Rh}_2(\text{OAc})_4$, carbenoid insertion into **1c** exclusively occurred to give **2c** in 60%, while hexyltrimethylsilane was completely recovered unchanged.¹¹ This result strongly suggests that the rigid conformation of a cyclic system plays an important role in activating the β C–H bond toward carbenoid insertion (vide infra).

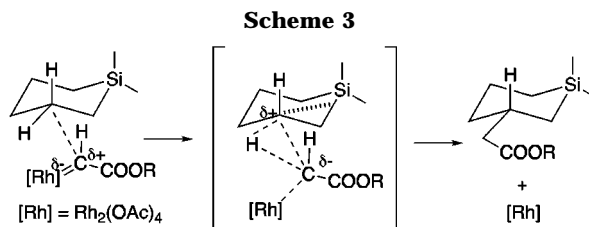
Utility of this chemistry is illustrated by the synthesis of γ -lactones starting from silacyclobutane derivative **2a** (Et), whose two Si–C bonds can be effectively utilized for achieving C–C and C–O bond formations (Scheme 2). Thus, the palladium-catalyzed ring-opening coupling reaction of **2a** (Et) with acid chlorides^{1e} gave quantitative yields of cyclic silyl enol ethers **3**, which can be used in the next step without further purification.¹² The oxidation of the C–Si bonds of **3** by H_2O_2 under the basic conditions¹³ afforded the corresponding γ -lactones **4** bearing a ketone functionality at the C3 position in good to excellent overall yields (73–94%).

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(11) In the absence of **1c**, hexyltrimethylsilane reacted with *tert*-butyl diazoacetate under catalytic conditions to give the corresponding β C–H bond insertion product in 36% yield.

(12) Under the same reaction conditions, less strained silacycloalkanes such as **1b** and **1c** did not react with benzoyl chloride.



The high regioselectivity observed in the Rh-catalyzed carbenoid insertion into silacycloalkanes would be explained by assuming a transition state depicted in Scheme 3. Overlap of the p-orbital of an electrophilic rhodium carbene¹⁴ with the σ -orbital of the reacting β C–H bonds of silacycloalkanes generates an electron-deficient three-center, two-electron transition state,¹⁵ in which developing positive charge on the β carbon can be neutralized by (σ – π) conjugation with the electron-donating Si–C bonds (β -effect);¹⁶ this stabilization of the partial positive charge on the β carbon by the Si–C bonds leads to an activation of the β C–H bonds toward carbenoid insertion.¹⁷ This hypothesis is strengthened by the fact that a silacycloalkane bearing an electronegative group on the silicon such as 1-methoxy-1-methyl-1-silacyclohexane failed to react with *tert*-butyl diazoacetate even at the elevated temperature, presumably due to the decreased electron density of the Si–C bonds.

In summary, we have demonstrated that the Rh-catalyzed carbenoid insertion into the β C–H bonds of silacycloalkanes provides a facile and general approach to functionalized silacycloalkanes, which proved to be useful precursors for the synthesis of γ -lactones having a ketone functionality at the C3 position. The exceptionally high regioselectivity of these reactions can be explained in terms of stabilizing interaction between the reacting β C–H bonds and the electron-donating Si–C bonds. We are currently studying the applications of functionalized silacycloalkanes in organic synthesis as well as in polymer synthesis.

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Supporting Information Available: Experimental details and characterization data for all new compounds (8 pages).

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(17) The observed low reactivity of hexyltrimethylsilane is attributable to the free rotation around the C(α)–C(β) bonds, which hinders the coplanarity between the empty p-orbital and the Si–C bonds to hamper the effective (σ – π) conjugation.¹⁶