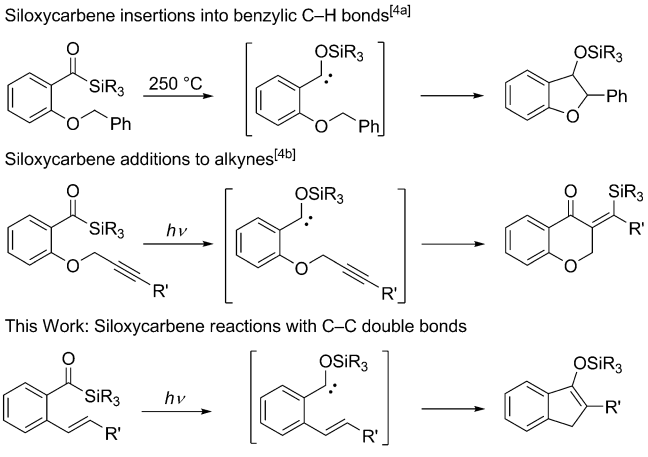
DOI: 10.1002/ange.201307446

Photochemistry

Acylsilanes in Rhodium(III)-Catalyzed Directed Aromatic C–H Alkenylations and Siloxycarbene Reactions with C–C Double Bonds[**]

*Peter Becker, Daniel L. Priebbenow, Ramona Pirwerdjan, and Carsten Bolm**

Abstract: *Acylsilanes are known to undergo a 1,2-silicon-to-oxygen migration under thermal or photochemical conditions to form siloxycarbenes. However, there are few reports regarding the application of siloxycarbenes in organic synthesis and surprisingly, their reaction with C–C double or triple bonds remains virtually unexplored. To facilitate such a study, previously inaccessible aromatic acylsilanes containing an ortho-tethered C–C double bond were identified as suitable substrates. To access these key intermediates, we developed a new synthetic method utilizing a rhodium-catalyzed oxidative Heck-type olefination involving the application of an acylsilane moiety as a directing group. When exposed to visible-light irradiation, the ortho-olefinated acylsilanes underwent a smooth intramolecular cyclization process to afford valuable indanone derivatives in quantitative yields. This result paves the way for the development of new transformations involving siloxycarbene intermediates.*



Scheme 1. Addition and insertion reactions of siloxycarbenes.

The insertion of a carbene into a C–H bond is a direct approach to the formation of a new C–C bond.[1] However, the current methods for accessing such reactive species are limited, and these transformations predominantly utilize diazocarbonyl compounds for the generation of the requisite carbenes. Acylsilanes are known to undergo 1,2-silicon-to-oxygen migration (known as the Brook rearrangement[2]) under thermal or photochemical conditions to form siloxycarbenes.[3] Although such processes appear synthetically attractive, only a limited number of reports regarding the application of acylsilanes as carbene precursors have been published.[4]

Recently, Shen and Dong reported insertions of siloxycarbenes, which were thermally generated under microwave irradiation, into benzylic C–H bonds to form substituted furans (Scheme 1, top).[4a] We have described light-induced additions of siloxycarbenes to C–C triple bonds and subsequent structural reorientations to give ketonic vinylsilanes (Scheme 1, middle).[4b] Unfortunately however, attempts to apply this strategy to analogous substrates with C–C double bonds have been unsuccessful.

To our knowledge, only a single example of a siloxycarbene addition to an alkene has been reported to date. In this case, a photochemically generated cyclic siloxycarbene was trapped by diethyl fumarate to afford an oxasila-[2.6]spirononane.[5] To allow a thorough investigation into the synthetic potential of such processes, the reaction of siloxycarbenes with an *ortho*-tethered C–C double bond on an arene was identified as an attractive transformation to study. If successful, this approach would be completely atom economic in leading to valuable indene scaffolds (Scheme 1, bottom). We quickly realized, however, that our initial focus had to be on preparing the starting materials and finding a new, effective route to *ortho*-olefinated aromatic acylsilanes.

In recent years, significant progress has been achieved in rhodium(III)-catalyzed *ortho* functionalizations of aldehydes, ketones, carboxylic acids, esters, amides, amines, alcohols, and oximes by oxidative Heck-type olefinations of arenes with alkenes such as acrylates or styrenes.[6,7] Since acylsilanes are often considered as aldehyde or ketone analogues,[3a,b] we were intrigued by the possibility of preparing the desired *ortho*-olefinated aroylsilanes (see above) by utilizing the aforementioned rhodium catalysis. We herein report on the realization of this proposal, thus opening access to a wide range of previously inaccessible olefinic aroylsilanes in excellent yields through *ortho*-directed aromatic C–H olefination reactions.

For the initial attempts to functionalize an unsubstituted aroylsilane at the *ortho* position, phenyltrimethylsilyl ketone (**1a**) and *n*-butyl acrylate (**2a**) were chosen as starting materials. Unfortunately, under the standard reaction conditions as reported by Glorius and co-workers[6c,d] for the rhodium-catalyzed C–H functionalization of acetophenones by using [(RhCp*Cl$_2$)$_2$] in combination with AgSF$_6$ as catalyst and Cu(OAc)$_2$ as oxidant in *tert*-amylalcohol at 120 °C for

---

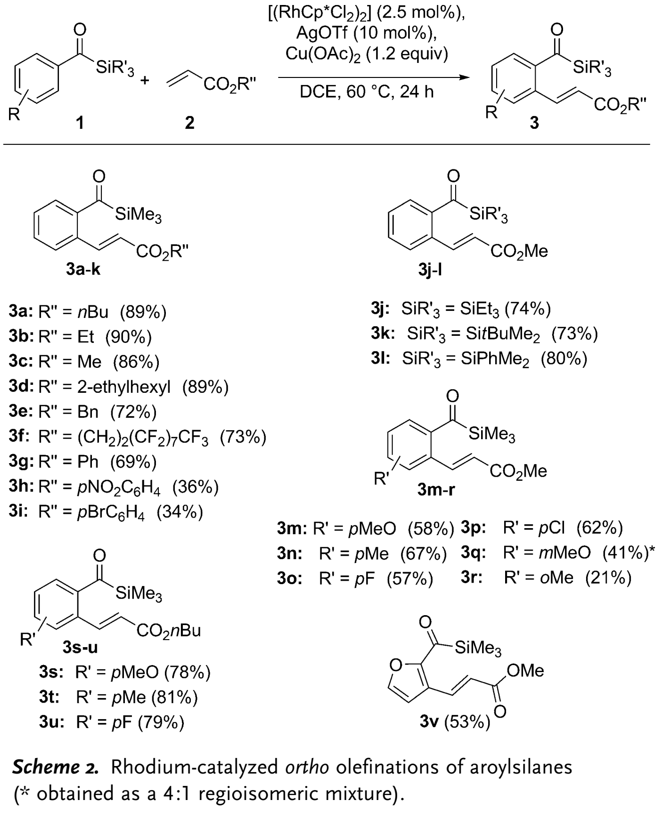
[*] P. Becker, Dr. D. L. Priebbenow, R. Pirwerdjan, Prof. Dr. C. Bolm
Institute of Organic Chemistry, RWTH Aachen University
Landoltweg 1, 52074 Aachen (Germany)
E-mail: carsten.bolm@oc.rwth-aachen.de

[**] D.L.P. acknowledges support by the Alexander von Humboldt foundation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201307446.

16 h, no product formation occurred. Changing the solvent to dichloroethane (DCE) led to the first positive result, providing *ortho*-olefinated aroylsilane **3a** in 6% yield. Subsequent optimization (see the Supporting Information for details) showed that neither toluene nor THF were suitable solvents, and that the use of AgOTf instead of $AgSF_6$ was beneficial. Furthermore, to avoid decomposition of the aroylsilane (to give benzaldehyde), both air and water had to be rigorously excluded and anhydrous $Cu(OAc)_2$ was employed as oxidant. At higher temperatures, a significant amount of 2,6-diolefinated product was observed. Improved yields were thus observed in the presence of a two-fold excess of the acrylate provided that the reaction temperature was lowered to 60 °C (and the reaction time extended to 24 h). Finally, we found that only 1.2 equiv of the oxidant were required (instead of the originally employed 2.5 equiv). Under the optimal reaction conditions (using $[(RhCp^*Cl_2)_2]$ (2.5 mol%), AgOTf (10 mol%), $Cu(OAc)_2$ (1.2 equiv) in DCE at 60 °C for 24 h) *ortho*-olefinated aroylsilane **3a** could be obtained (from **1a** and **2a** in a 1:2 ratio) in 89% yield (Scheme 2).

Next, the scope of the rhodium(III)-catalyzed olefination process was investigated (Scheme 2). The structure of the acrylic ester had only a minor effect on the cross-coupling. Hence, in reactions with **1a**, other aliphatic acrylic esters and those with a benzyl group or a highly fluorinated chain also worked well and afforded the corresponding products in high yields (Scheme 2, products **3b–f**; up to 90%). The use of aromatic esters led to slightly lower yields (Scheme 2, products **3g–i**; up to 69%). Unfortunately, styrene did not react with **1a**, and with a piperidine-derived acrylamide only a trace of product was obtained.



Scheme 2. Rhodium-catalyzed *ortho* olefinations of aroylsilanes (* obtained as a 4:1 regioisomeric mixture).

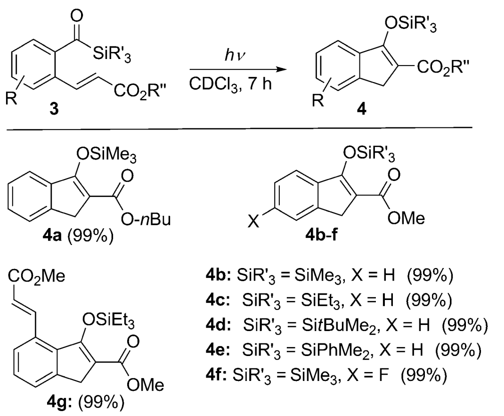
Next, the silyl moiety of the aroylsilane was varied using methyl acrylate (**2c**) as the coupling partner. In all cases, good yields were achieved (Scheme 2, products **3c** and **3j–l**; up to 86%). Apparently, steric effects at the silyl group had only a minor effect on the catalysis, a result consistent with the assumption that the rhodium catalyst is coordinated through the carbonyl group of the aroylsilane with the silyl group pointing away from the C–H bond undergoing metal insertion.

Changing the steric and electronic properties of the arene had only a minor effect on the cross-coupling. Although arenes bearing electron-donating substituents appeared to show enhanced reactivity, thus leading to more of the 2,6-diolefinated aroylsilanes, substrates with both electron-donating and electron-withdrawing groups provided products in almost the same yields (Scheme 2, products **3m–u**; up to 81%). The low yield (21%) obtained for **3r** indicates a steric effect when *ortho*-substituted substrates were applied. In general, reactions between the aroylsilanes and methyl acrylate (**2c**) led to slightly lower yields than those with *n*-butyl acrylate (**2a**; Scheme 2, products **3m–o** versus **3s–u**). A heteroaroylsilane also performed well, affording olefinated furan **3v** in 53% yield.

Two points should be commented on: First, compared to aldehydes and ketones, the analogous acylsilanes show enhanced reactivity in rhodium-catalyzed cross-coupling reactions, as indicated by the lower reaction temperature (120 °C versus 60 °C) required to allow the desired *ortho* olefination to proceed. We attribute this effect to the nature of the silicon–carbon bond in the latter compounds, which leads to an enhanced negative polarization at the carbonyl oxygen atom. This enhanced polarization facilitates metal coordination and rhodium insertion into the neighboring C–H bond. Second, owing to the fact that aldehydes tend to form carboxylic acids under the oxidative conditions required for the olefination process, and considering possible catalyst poisonings by extruded CO stemming from decarbonylative processes, only a few *ortho* olefinations of aldehydes are known.[7] The *ortho*-olefinated aroylsilanes prepared here could prove valuable in this respect, since acylsilane-to-aldehyde conversions are well-established.[3,8,9]

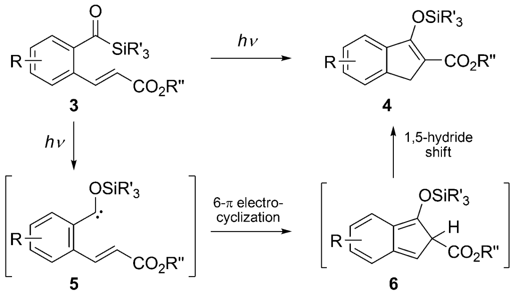
With suitable substrates for the envisaged intramolecular reaction of a photochemically generated siloxycarbene and a C–C double bond in hand, solutions of the aroylsilanes in deuterated chloroform were irradiated (in NMR tubes) using a common daylight energy-saver light bulb.[10] To our delight, a cyclization process occurred, thus leading to silyl enol ethers of indanones as sole products with complete atom efficiency (Scheme 3). In all cases, full conversions were observed (by NMR spectroscopy) independent of the electronic nature of the arene or the sterics of the silyl group. No further product purification was necessary. Methyl and *n*-butyl esters cyclized equally well (products **4a** and **4b**), and the reaction of a 2,6-diolefinated substrate was also successful, leading to full conversion into indanone **4g**.

Mechanistically, we propose that the aroylsilanes **3** undergo photochemically-induced Brook rearrangements to



Scheme 3. The light-induced cyclization of *ortho*-olefinated aroylsilanes affording silyl enol ethers of indanones (% values refer to yields as measured by NMR spectroscopy).

give siloxycarbenes **5**, followed by 6-π electrocyclizations and 1,5-hydride shifts to afford the observed silyl enol ethers **4** (Scheme 4). The pronounced difference in reactivity between aroylsilanes and the related aromatic aldehydes is noteworthy since UV-light-induced cyclizations of the latter compounds resulted in polycyclic isochromanones or four-membered cyclic ketones.[11]



Scheme 4. Proposed mechanism for the light-induced cyclization of *ortho*-olefinated aroylsilanes to afford silyl enol ethers **4**.

In summary, we have discovered rhodium(III)-catalyzed *ortho*-directed olefinations of aroylsilanes and demonstrated light-induced intramolecular cyclizations to indanone derivatives via photochemically generated siloxycarbenes. Both processes are high-yielding and extensions of this chemistry are currently ongoing.

Experimental Section

Rhodium-catalyzed olefination process: [(Cp*RhCl$_2$)$_2$] (0.01 mmol, 6.2 mg, 2.5 mol%), AgOTf (0.04 mmol, 10.3 mg, 10 mol%), Cu(OAc)$_2$ (0.48 mmol, 87.2 mg, 1.2 equiv), and dry DCE (0.5 mL) were added into a Schlenk tube under an argon atmosphere at room temperature. After 5 min of stirring, the aroylsilane (0.4 mmol, 1.0 equiv) followed by the acrylate (0.8 mmol, 2.0 equiv) was added. The reaction was heated to 60 °C and stirred for 24 h. After this time, the reaction mixture was filtered through a short plug of SiO$_2$ and washed with Et$_2$O, and the product was purified by SiO$_2$ column chromatography (10:1, pentane/EtOAc). (For additional experimental details, see the Supporting Information.)

Light-induced cyclization: The olefinated aroylsilane (0.2 mmol) was dissolved in deuterated chloroform (1 mL) and transferred into an NMR tube. The NMR tube was then irradiated by using a 23 W compact fluorescent lamp for 7 h at ambient temperature. (Note, owing to the heat emission of the lamp, the temperature rose to ca. 35 °C.) After the reaction was complete, the solution was directly measured by NMR spectroscopy to analyze the product.

Received: August 23, 2013

Keywords: acylsilanes · carbenes · C–H functionalization · photochemistry · rhodium catalysis

---

[1] a) H. M. L. Davies, R. E. J. Beckwith, *Chem. Rev.* **2003**, *103*, 2861; b) Z. Zhang, J. Wang, *Tetrahedron* **2008**, *64*, 6577; c) H. M. L. Davies, A. R. Dick in *C–H Activation, Vol. 292* (Eds.: J. Q. Yu, Z. Shi), Springer, Berlin, **2010**, p. 303; d) Q. Xiao, Y. Zhang, J. Wang, *Acc. Chem. Res.* **2013**, *46*, 236; e) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417.

[2] a) A. R. Bassindale, A. G. Brook, J. Harris, *J. Organomet. Chem.* **1975**, *90*, C6; b) A. G. Brook, *Acc. Chem. Res.* **1974**, *7*, 77.

[3] a) H. J. Zhang, D. L. Priebbenow, C. Bolm, *Chem. Soc. Rev.* **2013**, *42*, 8540; b) A. F. Patrocínio, P. J. S. Moran, *J. Braz. Chem. Soc.* **2001**, *12*, 7.

[4] a) Z. Shen, V. M. Dong, *Angew. Chem.* **2009**, *121*, 798; *Angew. Chem. Int. Ed.* **2009**, *48*, 784; b) H.-J. Zhang, P. Becker, H. Huang, R. Pirwerdjan, F.-F. Pan, C. Bolm, *Adv. Synth. Catal.* **2012**, *354*, 2157; c) K. Ito, H. Tamashima, N. Iwasawa, H. Kusama, *J. Am. Chem. Soc.* **2011**, *133*, 3716.

[5] A. G. Brook, H. W. Kucera, R. Pearce, *Can. J. Chem.* **1971**, *49*, 1618.

[6] For selected recent contributions, see: a) S. Mochida, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2011**, *76*, 3024; b) T. Iitsuka, P. Schaal, K. Hirano, T. Satoh, C. Bolm, M. Miura, *J. Org. Chem.* **2013**, *78*, 7216; c) F. W. Patureau, T. Besset, F. Glorius, *Angew. Chem.* **2011**, *123*, 1096; *Angew. Chem. Int. Ed.* **2011**, *50*, 1064; d) S. Rakshit, C. Grohmann, T. Besset, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2350; e) H. Li, Y. Li, X.-S. Zhang, K. Chen, X. Wang, Z.-J. Shi, *J. Am. Chem. Soc.* **2011**, *133*, 15244; f) C. Wang, H. Chen, Z. F. Wang, J. A. Chen, Y. Huang, *Angew. Chem.* **2012**, *124*, 7354; *Angew. Chem. Int. Ed.* **2012**, *51*, 7242; g) B. Liu, Y. Fan, Y. Gao, C. Sun, C. Xu, J. Zhu, *J. Am. Chem. Soc.* **2013**, *135*, 468.

[7] a) S. H. Park, J. Y. Kim, S. Chang, *Org. Lett.* **2011**, *13*, 2372; b) F. Kakiuchi, T. Sato, K. Igi, N. Chatani, S. Murai, *Chem. Lett.* **2001**, 386; c) N. Gürbüz, I. Özdemir, B. Çetinkaya, *Tetrahedron Lett.* **2005**, *46*, 2273.

[8] a) D. Schinzer, C. H. Heathcock, *Tetrahedron Lett.* **1981**, *22*, 1881; b) A. G. Brook, *J. Am. Chem. Soc.* **1957**, *79*, 4373; c) A. G. Brook, J. M. Duff, *J. Am. Chem. Soc.* **1967**, *89*, 454; d) S. E. Denmark, M. Xie, *J. Org. Chem.* **2007**, *72*, 7050.

[9] Note that experiments with [{Ru(*p*-cymene)Cl$_2$}$_2$] in *tert*-amyl alcohol afforded the olefinated aldehyde as the sole product (Table S1, entry 6, in the Supporting Information).

[10] A 23 W Philips Genie energy-saver daylight lamp (2700 K) was used.

[11] a) W. Xia, Y. Shao, W. Gui, C. Yang, *Chem. Commun.* **2011**, *47*, 1098; b) K. Padala, M. Jeganmohan, *Org. Lett.* **2012**, *14*, 1134.