Tetrahedron 70 (2014) 4232–4244

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

An analysis of the influences dictating regioselectivity in platinum-catalyzed hydrosilylations of internal alkynes

Douglas A. Rooke, Zachary A. Menard, Eric M. Ferreira *

Department of Chemistry, Colorado State University, Fort Collins, CO 80523, United States

ARTICLE INFO

Article history:
Received 16 January 2014
Received in revised form 1 March 2014
Accepted 4 March 2014
Available online 13 March 2014

Keywords:
Hydrosilylation
Alkyne
Catalysis
Platinum
Regioselectivity

ABSTRACT

A full account of our studies on internal alkyne hydrosilylations using platinum catalysis is described. We demonstrate that these transformations are highly governed by the electronic characteristics of the alkyne substituents, wherein the hydride will add preferentially to the more electron-deficient alkyne carbon. The steric and coordinative capabilities of the substituents influence the selectivity to a much lesser extent, with propargylic alcohols a lone exception. The choice of silane is relevant in some cases; specific silanes will afford high regioselectivities while others are much less selective. Ultimately, the regioselectivity of addition can be quite predictable using ^{13}C NMR chemical shift data, allowing this reactivity to be incorporated into purposeful reaction design.

1. Introduction

The metal-catalyzed hydrosilylation reaction of alkenes and alkynes is a well-studied transformation.[1] Vinylsilanes, the products of alkyne hydrosilylation, can serve as useful precursors for Tamao–Fleming oxidations,[2] nucleophilic additions,[3] Hiyama couplings,[4] and halodesilylation reactions.[5] The widespread synthetic use of vinylsilanes rests upon the ability for their syntheses to be facile with high regio- and stereocontrol. An overwhelming majority of research on alkyne hydrosilylation has focused on the anti-Markovnikov addition of a silane across a terminal alkyne, a transformation that has reliably provided the terminal silane. Conversely, internal alkynes have received considerably less attention, which can be at least partially attributed to the difficulty of achieving regioselective transformations with this substrate class (Fig. 1).

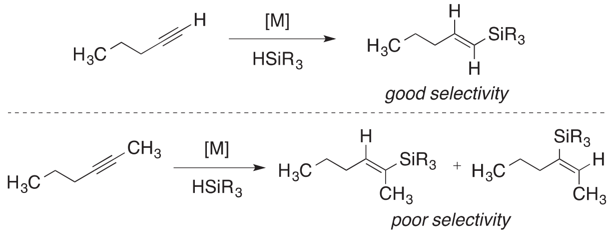


Fig. 1. Contrasting hydrosilylations of terminal and internal alkynes.

Our entry into the field of metal-catalyzed hydrosilylations began with our desire to obtain (*E*)-α-silylenones, the geometric isomers of the products of our platinum catalyzed 1,2-silyl migration reaction of α-hydroxypropargylsilanes.[6] To our delight, this class of internal alkyne substrates afforded excellent regio- and stereoselectivity in catalytic hydrosilylation. We sought to fully understand the effects that influenced this process and its characteristic selectivity, and we previously reported several aspects our findings.[7] Herein, we present a comprehensive account of our study, illustrating how regioselective hydrosilylations of internal alkynes can be accomplished depending on the nature of the two alkyne substituents.

1.1. Background

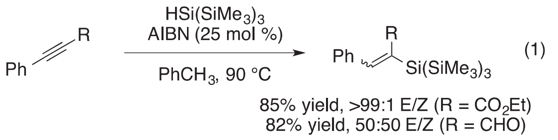
There are many different methods reported to afford hydrosilylation products. However, the selectivity of Si–H addition can be a limitation of further synthetic utility for these methods. Radically induced hydrosilylation requires a silane that can easily undergo homolytic cleavage of the Si–H bond (Eq. 1).[8] The intermediate vinyl radical of this silane addition can be configurationally labile. High stereoselectivities have been achieved in certain cases, but for others the process is less effective. Lewis acids like $AlCl_3$ can

---

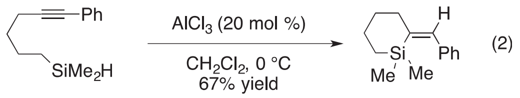
* Corresponding author. Tel.: +1 970 491 6379; fax: +1 970 491 1801; e-mail addresses: emferr@mail.colostate.edu, eric.ferreira@colostate.edu (E.M. Ferreira).

0040-4020/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2014.03.012

catalyze the trans addition of a hydrosilane across an alkyne (e.g., Eq. 2).[9]



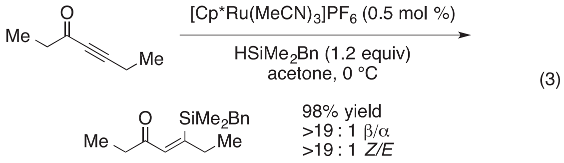
(1)



(2)

The strong Lewis acids that promote this transformation, however, can also catalyze the isomerization of the alkene. Early transition metal complexes, such as titanocene[10] and organoyttrium compounds[11] have been shown to catalyze the cis-addition of a silane across an alkyne. Due to issues primarily related to regioselectivity and functional group tolerance, the abovementioned methods of hydrosilylation have received little attention in the context of synthetic utility. Conversely, late transition metals have been the primary focus of research in regard to hydrosilylation.

The hydrosilylation chemistry catalyzed by late transition metals is both diverse and well-documented. Two separate mechanisms are cited for the observed regioselectivity of the hydrosilylation. One mechanism (the Crabtree–Ojima mechanism) has been observed in several cases using late transition metal catalysts based on Rh, Ir, and Ru.[12] This mechanism proceeds via a metallocarbene species, which leads to possible *E*/*Z* isomerizations. An exceptional catalytic system based on this mechanism, Trost and Ball have shown that CpRu(MeCN)$_3$PF$_6$ catalyzes an exclusively trans addition of silane with excellent selectivity and for a wide variety of internal alkynes (Eq. 3).[13]



(3)

Pt-catalyzed hydrosilylations, alternatively, generally proceed though the standard Chalk–Harrod mechanism,[14] which provides complementary *syn*-addition products. Platinum and palladium catalysts are widely used for these hydrosilylation reactions and generally give products arising from the cis-addition of silane across an alkyne. In 1957, Speier was the first to report platinum-catalyzed hydrosilylations using H$_2$PtCl$_6$ (now termed Speier's Catalyst).[15] Today this catalyst is one of the most commonly used hydrosilylation catalysts in an industrial setting. The cis selectivity of addition is reflective of the Chalk–Harrod mechanism for Pt hydrosilylation (Fig. 2), wherein Pt(II) coordinates to an olefin (later applied to alkynes), and oxidative addition of the silane occurs. The resulting Pt(IV) complex undergoes migratory insertion across an olefin or alkyne, delivering a hydride to one of the two carbons. The resulting C–Pt–Si complex can then undergo reductive elimination to afford the cis hydrosilylation products.

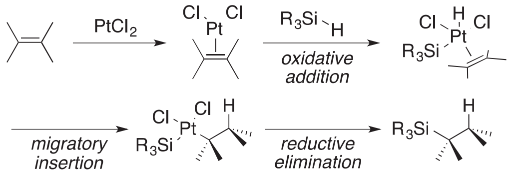


Fig. 2. The Chalk–Harrod mechanism for metal-catalyzed hydrosilylation.

The Chalk–Harrod mechanism has been widely accepted and can generally be applied to platinum-based hydrosilylation reactions. However, a number of phenomena are still unexplained by this mechanism. First, the other widely used catalyst in hydrosilylation is Karstedt's catalyst, a Pt(0)–divinyldisiloxane complex, which may implicate a similar catalytic mechanism invoking Pt(0) and Pt(II) oxidation states.[16] Second, it has been shown that alternative operational platinum catalysts, such as Pt(cod)Cl$_2$, are not active but instead are precatalysts that must undergo an induction period. Roy and Taylor have studied this induction period in depth and have concluded that the classical Chalk–Harrod mechanism can proceed through both Pt(II)–Pt(IV) and Pt(0)–Pt(II) catalytic cycles.[17] As long as the Chalk–Harrod mechanism holds, we can presume that the hydride is delivered during the migratory insertion step, and this step is thus playing a significant role in determining the regioselectivity and stereoselectivity of the net hydrosilylation.

Today, regioselective hydrosilylation on internal alkynes remains difficult, and research efforts have often focused on exploiting sterics dictated by both the substrate and catalyst system. Markó and co-workers have performed extensive work on the hydrosilylation of alkynes using bulky Pt/NHC catalysts developed in their lab.[18] Although chiefly focused on terminal alkynes, a number of internal alkynes were also investigated with some providing high regioselectivities. In 2011, Cook developed an active catalytic system for the hydrosilylation of propargylic alcohols.[19] Predictably, terminal alkynes showed excellent selectivity, while internal alkynes were much less selective unless significant steric bulk was employed to influence the addition. A recent report from Hosoya and co-workers illustrates Pd-catalyzed hydrosilylations of electron-deficient alkynes, where high regioselectivities have been achieved.[20] There have also been a few isolated examples where the alkyne electronic influence has been observed, often in substrate syntheses or specialized cases.[21]

The notion that electronic effects can dictate alkyne hydrosilylation was introduced by Tsipis in 1980. He hypothesized that the polarization of an alkyne would direct the hydride addition to the more electropositive carbon.[22] Up until this point, since most hydrosilylation centered around terminal alkynes and alkenes, sterics were believed to be the single most contributing factor affecting regioselectivity. Tsipis noted that the magnitude of difference in ^{13}C chemical shifts for terminal alkynes is rather large (~15–20 ppm).[23] However, for internal alkynes, the difference in alkyne chemical shifts is markedly less (approximately 3–5 ppm). These data could serve as predictors for which alkyne carbon has the lowest lying LUMO. He therefore posited that the hydrosilylation regioselectivity was impacted by this polarization in addition to the steric effects (Fig. 3).

Alami and co-workers, in their investigations of *ortho*-substituted arylacetylenes, showed one of the most salient first examples of highly selective internal alkyne hydrosilylation using PtO$_2$ (Fig. 4).[24] Interestingly, it was found that almost any substituent, from −NO$_2$ to −*i*-Pr, induced selectivity for the α-silyl isomer. This occurrence was observed even for cases involving diarylacetylenes—the silicon species will preferentially add to the alkyne carbon bearing the *ortho*-substituted aryl group.

More telling of the absolute electronic effects of this silane addition were their analyses of *para*-substituted diarylacetylenes (Fig. 5). Both alkyne carbons of these diarylacetylenes should have similar steric environments, and the *para*-substituent should exert a negligible coordinative effect. Therefore, any addition selectivity would likely be a consequence of alkyne polarization. In comparing