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## COMMUNICATION

## Highly selective hydrosilylation of equilibrating allylic azides

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The Pt-catalyzed hydrosilylation of equilibrating allylic azides is reported. The reaction provides only one out of four possible hydrosilylation products in good yields and with very high chemoselectivity (alk-1-ene vs alk-2-ene), regioselectivity (linear vs branched), and excellent functional group tolerance.

The rearrangement of allylic azides, which is first discovered by Winstein and co-workers in 1960, provides an interesting platform for studying the relative reactivity of different types of azides and olefins.<sup>1</sup> However, this rearrangement generally produces a mixture of constitutionally isomeric allylic azides consisting of alk-1-ene isomer featuring the secondary azide as well as trans- and cis-alk-2-ene isomers both featuring the primary azide (Fig. 1, top). Thus, this reaction has seen limited synthetic applications because of the generation of mixtures of olefin and azide products, thereby prohibiting subsequent transformations.<sup>2,3</sup> In order to achieve the selective capture of alk-1-ene isomer in the downstream reactions,  $k_3$  and  $k_2$  must be much faster than  $k_1$  (Fig. 1, top). At the same time, the relative difference between  $k_2$  and  $k_3$  is less significant than that of  $k_1$ , while the branched alk-1-ene isomer is considerably more useful than either of the linear alk-2-ene isomers. For metalcatalyzed reactions, the strong coordination of the azide group makes metal binding easier than the alternative binding of the metal to the olefin or other reactive partners (Fig. 1., top). This in turn inhibits the catalytic cycle, greatly increasing the difficulty of achieving synthetically useful selectivity in allylic azide rearangement reactions. Although allylic azide isomers have been successfully differentiated in intramolecular reactions by tuning the distance between a reactive site and azide/olefin,<sup>4</sup> the selectivity in significanlty more synthetically valuable intermolecular reactions of allylic azides has not been accomplished to date. <sup>5</sup> These reactions could lead to the



synthesis of nitrogen-functionalized alk-1-ene derivatives that would be difficult to access by existing methods. For example, the difference between primary and secondary azides in allylic azide isomers cannot be distinguished in the azide-alkyne cycloaddition reaction (AAC) (Fig. 1, bottom), while the more electron-rich nature of disubstituted than monosubstituted olefin has been exploited in epoxidation reactions.<sup>5a</sup> Furthermore, in the palladium-catalyzed Wacker oxidation of allylic azide isomers, the derivatized product of alk-1-ene isomer has been observed; however, this azidoaldehyde is

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unstable, leading to the overall low selectivity of the rearrangement (Fig. 2, bottom).<sup>5b,6</sup> Thus, the selective capture of one of the allylic azide isomers, especially the synthetically more useful branched alk-1-ene isomer, in an intermolecular downstream reaction would significantly improve the synthetic applicability of allylic azides. More importantly, the selective differentiation of alk-1-ene over alk-2-ene of allylic azide mixtures in a subsequent olefin hydrofunctionalization<sup>7</sup> would provide very useful functionalized secondary azides, which typically require multiple steps by conventional methods.<sup>8</sup>

Herein, we report that differentiating the reactivity of alk-1ene over alk-2-ene can be achieved by merging the allylic azide rearrangement with olefin hydrosilylation. Strikingly, equilibrating allylic azides afford one out of the four possible hydrosilylation products in this novel process.

The alkene hydrosilylation is one of the most industrially used transformations for upgrading commodity alkenes.<sup>7</sup> Among various catalysts, Pt-based complexes are employed most frequently due to their high reactivity, good anti-Markovnikov selectivity, and broad functional group compatibility.<sup>9</sup> Among many challenges to achieve high selectivity in hydrosilylation of equilibrating allylic azides, the catalytic system must be compatible with the sensitive azide group.<sup>10</sup> It is well known that azides can react with most transition metals to form imido complexes, thus inhibiting the catalytic turnover.<sup>11</sup> Moreover, widely used phosphine ligands in transition-metal-catalysis can react with azides, e.g. Staudinger reaction, thus losing their ability to tune the transition metal.<sup>12</sup> These challenges are exacerbated because of the temperatures required in order to accelerate the allylic azide rearrangement.1c,3 Thus, the successful implementation of selective hydrosilylation of equilibrating allylic azides heavily relies on the compatibility between the catalytic system and the allylic azide as well as the faster hydrosilylation rate of alk-1-ene than alk-2-ene, whereas the linear/branched selectivity must also be considered.

As shown in Table 1, alkene 1 was reacted with allyl bromide via alkene cross metathesis using the Hoveyda-Grubbs catalyst 2nd generation (HG-2) to give the corresponding allylic bromide, which without purification was subjected to the subsequent azide displacement to afford trans-alk-1-ene 2a, which rapidly rearranged at room temperature and reached a steady-state equilibrium of allylic azides with 60:10:30 ratio of three constitutional isomers 2a, 2b, and 2c.4b Initially, we conducted the hydrosilylation of allylic azdie 2 catalyzed by the Co(acac)2/xantphos system without any reaction, while the deazidation mixture of 1-alkene and 2-alkene was obtained by the Fe/OIP-catalyzed hydrosilylation.13 Then we turned our attention to Pt-based Karstedt's catalyst, which has been used as a benchmark in many industrial hydrosilylations.9 The reaction of 2 with 4.0 equiv of tertiary silane PhMe<sub>2</sub>SiH was carried out with 5 mol% of Karstedt's catalyst at 90 °C, and afforded 76% of 3c, the anti-Markovnikov hydrosilylation product (entry 1, Table 1). Remarkably, we did not observe 3a, resulting from hydrosilylation of 2a or 2b,14 nor 3b, the Markovnikov hydrosilylation product of 2c (<sup>1</sup>H NMR analysis). The overall yield of 76% exceeded the percentage (30%) of 2c in

Table 1 Preparation and selective hydrosilylation of equilibrating allylic azides.<sup>a</sup>

Bn 1	1. HG-2 allyl bromide 2. NaN <sub>3</sub> 60%	Bn trans-Alk-2-ene: 2a cis-Alk-2-ene: 2b $\downarrow k_5$ N <sub>3</sub> Bn Alk-1-ene: 2c mixture 2a:2b:2c = 60:10:30 <sup>15</sup>	Catalyst, PhMe <sub>2</sub> SiH	: 10.10. Bn Bn Bn	39/D0CC01310 SIMe <sub>2</sub> Ph 3a N <sub>3</sub> 3b SIMe <sub>2</sub> Ph	6
Entry	Catalyst	Cat. Loading (mol%)	Solvent	Yield of <b>3c</b> (%) <sup>c</sup>	Ratio <b>3c:(3a+3b)</b> <sup>d</sup>	1
1	Karstedt's cat.	5	THF	76	> 30:1	
2	(COD)PtCl <sub>2</sub>	10	Toluene	70	> 30:1	
3	Pt(dba)₃	1.5	MTBE	71	> 30:1	
4	$H_2PtCl_4 \cdot 6H_2O$	10	Toluene	28	> 30:1	
5	$K_2PtCl_4$	10	Toluene	65	> 30:1	
6	Marko's cat.	2	Toluene	58	> 30:1	
7	Karstedt's cat.	0.25	Toluene	86 <sup>e</sup>	> 30.1	

 $^a$  Conditions: 2 (0.3 mmol), PhMe2SiH (4.0 equiv.), solvent (2.5 mL), 90 °C, 36 h.  $^b$  Determined by  $^1H$  NMR in CDCl3.  $^c$ Isolated yield.  $^d$  Only one isomer observed by  $^1H$  NMR.  $^c$  70 °C, 24 h.



the starting allylic azide **2**, thus indicating that  $k_4$  and  $k_6$  must be much slower than  $k_7$ . These results demonstrate that the rate differentiation of alk-1-ene over alk-2-ene is realized in the hydrosilylation of equilibrating allylic azides. Examination of other Pt-based complexes, such as (COD)PtCl<sub>2</sub>, Pt(dba)<sub>3</sub>, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, K<sub>2</sub>PtCl<sub>6</sub> and even Marko's catalyst,<sup>15</sup> gave lower yields (entries 2-6, Table 1). After further screening (Table S1, ESI), 0.25 mol% of catalyst loading was established as optimal (entry 7, Table 1). Importantly, this suggests that the azide group influences the efficiency of catalyst only to some extent in comparison to the reported olefin hydrosilylation.<sup>16</sup> This reaction underwent smoothyl on 5 mmol scale to afford **3c** in 84% isolated yield.

With the optimal reaction conditions established, we examined the substrate scope of this novel protocol (Scheme 1). Importantly, in all cases, only one linear regioisomer in this hydrosilylation was observed out of the three or four interconverting allylic azide isomers. After simple conversion to allylic azides, feedstock olefins were transformed into functionalized 3-azidopropansilanes 4-9 in good yields. The reaction is compatible with a wide range of functional groups, including internal olefins (10), ketones (11, 12, 26, 28), esters (13, 14, 15, 26), amides (16), carboxylic acids (17), ethers (18), azides (19), tosyl amides (20, 21), imides (22), epoxides (23, 24, 25), and even ketals (27). The diastereoselectivity resulting from the existing stereocenters (10, 23-28) is low when the newlybuilt azido stereocenter is adjacent to the existing stereocenter (23). Modest selectivity is observed for 27 when methyl group was introduced at the 2-position of allylic azides. Importantly,

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only one ison 4-36 yield (dr)<sup>b</sup>

85%

N<sub>3</sub>

**13** 97%

25

35% (1:1:1:1 dr)<sup>G</sup>

NR

SiMe<sub>2</sub>Ph

SiMe-

SiMe<sub>2</sub>Ph

EtC

19

81%

EtOOC



2. benzoyl chloride SiMe<sub>2</sub>Ph SiMe<sub>2</sub>Ph Et<sub>3</sub>N, DCM 39 3c 70% Ph CuSO4.5H2O 1. HBF<sub>4</sub>·Et<sub>2</sub>O, DCM, sodium L-ascorbate 0 °C, 12 h *t*BuOH/H<sub>2</sub>O (1:1) 12 h, 71% 2. KF, H<sub>2</sub>O<sub>2</sub>, NaHCO<sub>3</sub>, MeOH/THF, 12 h, rt 58% SiMe<sub>2</sub>Ph Ph 38 37 Scheme 2 Conversions of 3-azidopropylsilane 3c

this protocol can be used to modify complicated drug molecules. For example, estrone was converted to the siliconfunctionalized azide 28 in 63% yield.

For most allylic azides, the ratio of alk-1-ene isomer ranges from 6% (S21) to 48% (S25), and is influenced by adjacent substituents (Table S2, ESI). When the substituent is larger and closer to the allylic azide moiety, the ratio of alk-1-ene isomer drops (e.g. 23 vs. 24). The introduction of groups at the 2position of allylic azides significantly increases the ratio of alk-1-ene isomer (e.g. 27). The allylic azide rearrangement is prevented by conjugation with arenes or carbonyl derivatives, such as when the hydrosilylation failed to afford 30 and 31 with

no reaction occured. Although the phenyl group at the 2position of allylic azides is still conjugated with the olefin, it doesn't influence the allylic azide rearrangement, leading to 29 in 50% yield. Examination of other tertiary silanes, such as triethylsilane, diphenylmethylsilane, triphenylsilane, triethoxylsilanes, and tert-butyldimethyl silane, resulted in the formation of the corresponding products 32-36 in high yields in all cases.

N<sub>3</sub>

8

57%

N<sub>2</sub>

14

55%

N<sub>3</sub>

20

69%

26

90% (1:1 dr)

ſSi

N<sub>3</sub>

32 81% ([Si] = Et<sub>3</sub>Si)

33 81% ([Si] = Ph2MeSi **34** 83% ([Si] = Ph<sub>3</sub>Si)

35 81% ([Si] = (EtO)<sub>3</sub>Si)

36 71% ([Si] = <sup>t</sup>BuMe<sub>2</sub>Si)<sup>d</sup>

COOEt

SiMe<sub>2</sub>Ph

To further demonstrate the synthetic utility of this new reaction, we utilized the copper-catalyzed AAC reaction to convert 3c into triazole 37 in 71% yield (Scheme 2).17 Next, hydrogenation and acylation afforded amide 39 in 70% yield. Finally, although conversion of silane to the hydroxyl group was initially problematic because of the low stability of the azide group to acidic conditions,<sup>18</sup> after short optimization (Table S3, ESI), 1,3-azido alcohol 38 was obtained in 58% yield along with 12% of 3-hydroxy ketone as the degradation product of azide group. These reactions clearly demonstrate the bi-functional properties of  $\gamma$ -azido-silanes produced in this tandem allylic azide rearrangement/hydrosilylation process.

In summary, the Pt-catalyzed hydrosilylation of equilibrating allylic azides provides only one out of four possible hydrosilylation products in good yields and with very high chemoselectivity (alk-1-ene vs alk-2-ene), regioselectivity (linear vs branched), and very good functional group tolerance.

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SiMe<sub>2</sub>Ph

SiMe<sub>2</sub>Ph

SiMe<sub>2</sub>P

 $N_3$ 

9

77%

N<sub>2</sub>

15

54%

N<sub>3</sub>

21

68%

**27** 79% (32:28:18:22 dr)

MeOOC

MeOOO

#### Journal Name

In combination with the facile preparation of allylic azides from simple and abundant olefins, this mild and general protocol provides rapid access to a diverse array of 3-azidopropylsilanes. These compounds serve as bi-functional handles featuring the versatile azide and silicon functional groups. Efforts to develop an asymmetric version of this reaction are currently underway in our laboratory.

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## **Conflicts of interest**

There are no conflicts to declare.

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