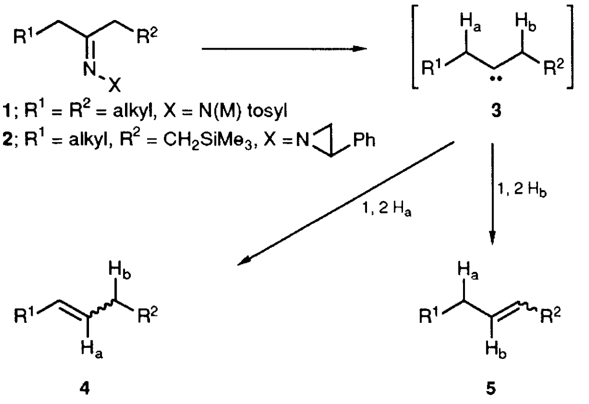
Silicon-directed Bamford–Stevens Reaction of β-Trimethylsilyl *N*-Aziridinylimines

Tarun K. Sarkar* and Binay K. Ghorai

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

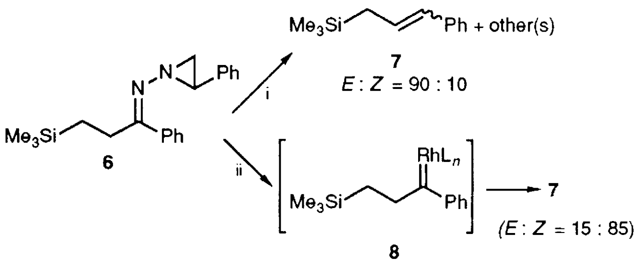
The Me_3Si group in β-trimethylsilyl *N*-aziridinylimines is able to direct the Bamford–Stevens reaction with or without rhodium acetate as catalyst to give allylic silanes as major or exclusive products.

Although the Bamford–Stevens reaction has been around for several decades, it has not generally proved useful for the synthesis of acyclic alkenes *via* thermal decomposition of metallated tosylhydrazones **1** in view of the indiscriminate 1,2-rearrangement of the carbenic intermediates **3** (Scheme 1) which results in a mixture of alkenes **4** and **5** and minor C–H insertion products, *e.g.*, cyclopropanes.[1] A considerable body of experimental evidence as well as theoretical calculations indicate that the migrating hydrogen (H_a or H_b) suffers an electrophilic pull from the vacant p-orbital of the singlet carbene centre in the transition state of this rearrangement.[2] It is thus conceivable that replacement of one of the alkyl groups (*e.g.* R^2) by a trimethylsilylmethyl group in **3** would enhance the migratory aptitude of H_b (β effect[3]) so that this hydrogen migration competes effectively with other C–H insertion reactions. The net result would be a tilt in favour of formation of allylsilanes **5** (R^1 = alkyl; R^2 = CH_2SiMe_3) over isomeric homoallylsilanes **4** (R^1 = alkyl; R^2 = CH_2SiMe_3). Herein we report that the Bamford–Stevens reactions of a number of β-trimethylsilyl *N*-aziridinylimines[4] **2** and derivatives are directed[5] by the trimethylsilyl group to give allylic silanes **5** as major or exclusive products.



Scheme 1

In contrast to α-[6] and more recently β-silyl carbenes[7] we found that significant C–H/C–Si[8] insertion reactions did not complicate the fate of simple γ-silyl carbenes, *e.g.*, **3** (R^1 = Ph; R^2 = CH_2SiMe_3) formed by thermal decomposition of **6**† to give after preparative TLC an inseparable mixture of the allylsilanes **7**‡ ($E:Z$ = 90 : 10) in 65% yield (Scheme 2) along with about 10% of a slightly polar (TLC) material which was not further characterized. Furthermore, the by-products accompanying **7** could be totally eliminated when the same reaction was run in presence of $Rh_2(OAc)_4$ (2 mol %) to yield **7** ($E:Z$ = 15 : 85) in 85% yield. The reversal of stereoselectivity in this case is explicable in terms of orientational



Scheme 2 *Reagents and conditions*: i, toluene, 145 °C, 2.5 h (sealed tube); ii, toluene, $Rh_2(OAc)_4$, 145 °C, 2.5 h (sealed tube)

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† All *N*-aziridinylimines reported in this paper were prepared in 82–95% yield by condensation of the respective β-silyl ketones with 1-amino-2-phenylaziridinium acetate in CH_2Cl_2 at 0 °C (3–4 h); see D. Felix, R. K. Muller, U. Horn, R. Joos, J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta*, 1972, **55**, 1276.

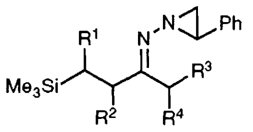
‡ Containing traces (3%) of an Me_3Si-containing material (^1H NMR) which is presumed to be an insertion product.

Table 1 Bamford–Stevens reaction of β-trimethylsilyl *N*-aziridinylimines

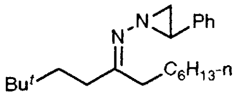
			Product ratio		
Entry	Imine[a]	Conditions[b]	Allylsilane **5** ($E:Z$)[c]	Homoallylsilane **4** ($E:Z$)[c]	Total yield[d,e] (%)
1	**9**	**A**	74(80 : 20)	26[f,g]	68
2	**9**	**B**	98(14 : 86)	2[f]	72
3	**10**	**A**	76(80 : 20)	24[f]	69
4	**10**	**B**	98(17 : 83)	2[f]	72
5	**11**	**A**	92(80 : 20)	8(75 : 25)	66
6	**11**	**B**	>99(14 : 86)	<1[f]	71
7	**12**	**A**	90(84 : 16)	10(75 : 25)	67
8	**12**	**B**	>99(13 : 87)	<1[f]	71
9	**13**	**A**	90(60 : 40)	10(75 : 25)	65
10	**13**	**B**	100(40 : 60)	0	82
11	**14**	**A**	70(86 : 14)	30[g]	62
12	**14**	**B**	67(29 : 71)	33[g]	80

[a] See footnote †. All β-silyl *N*-aziridinylimines are mixture of diastereoisomers and/or geometrical isomers. [b] **A** : a 5% solution of the substrate in toluene was heated at 145 °C for 3.5–4.5 h in a sealed tube under argon. **B** : a 5% solution of the substrate in toluene was heated at 145 °C for 3.5–4.5 h under argon in a sealed tube in presence of 2 mol % of $Rh_2(OAc)_4$. [c] Allylsilane : homoallylsilane ratios and $E:Z$ ratios were determined from ^1H NMR and/or capillary GC analysis. [d] Isolated yield of chromatographically pure products (homogeneous on TLC). [e] Products in entries 1, 3, 5, 7, 9 and 11 are contaminated with about 1–7% of a silicon-containing by-product (^1H NMR) which is presumed to be an insertion product. Also, 5–8% of a chromatographically separable but unidentified compound(s) accompanied the crude products in these runs. [f] $E:Z$ ratio not determined. [g] Presence of this product(s) was further confirmed by direct comparison (^1H NMR, capillary GC) with authentic samples.

constraints for hydrogen migration in the transient metal–carbene intermediate **8**.[9] This last experiment also showed that the use of rhodium acetate at 145 °C is not beyond the tolerance limit of this catalyst.



9; $R^1 = R^2 = R^4 = H$, $R^3 = n\text{-}C_6H_{13}$
10; $R^1 = R^2 = R^4 = H$, $R^3 = n\text{-}C_{11}H_{23}$
11; $R^1 = R^2 = R^4 = H$, $R^3 = CH_2Ph$
12; $R^1 = Me$, $R^2 = R^4 = H$, $R^3 = CH_2Ph$
13; $R^1 = R^4 = H$, $R^2 = Me$, $R^3 = CH_2Ph$
14; $R^1 = R^2 = H$, R^3, $R^4 = [CH_2]_4$



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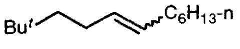

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A series of β-silylated *N*-aziridinylimines **9–14** was subjected to thermal decomposition under the foregoing catalytic and noncatalytic conditions and the results are summarized in Table 1.§ In the non-catalytic mode (entries 1, 3, 5, 7, 9 and 11), the directive effect of silicon can be clearly seen resulting in the predominant formation of allylsilanes (70–92%) over homoallylsilanes (8–30%). Entry 11 gives an idea of the magnitude of this effect where silicon overrides the normal reactivity pattern for intramolecular 1,2-migration (tert. > sec. >> prim.).[10] In the catalytic mode (entries 2, 4, 6, 8 and 10), in addition to the expected reversal in the *E–Z* stereoselectivity of the process, the nearly exclusive formation of allylsilanes and total elimination of the traces of by-products accompanying allylsilanes–homoallylsilanes in the noncatalytic runs is gratifying. The beneficial effect of silicon is most strongly evident in the rhodium ylides (*cf.* **8**) where the γ-carbon carries a transient positive charge and is in accord with the observation[11] that a silyl group attracts a cationic site from the γ- to the β-position. However, the somewhat diminished influence of silicon in entry 12 is not at present clearly understood. Finally, in order to establish that the silyl group is the powerful force in controlling regioselectivity of these reactions, a model system that has, for example, a *tert*-butyl group to replace the trimethylsilyl group was studied. To this end, **15** was subjected to Bamford–Stevens reaction in the presence of $Rh_2(OAc)_4$ (see Table 1) to give as expected an inseparable mixture of **16** and **17** in a ratio¶ of 43 : 57.

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§ All new compounds were fully characterized by NMR, IR, MS and/or microanalysis.

¶ This ratio was determined by oxidative cleavage ($RuO_2{\cdot}xH_2O$, $NaIO_4$) of **16** and **17** and careful ^1H NMR analysis of the product mixture as well as comparison with authentic samples.