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Formal [3+3]- and [3+2]-Cycloadditions of Allylsilanes with Benzylic Cations

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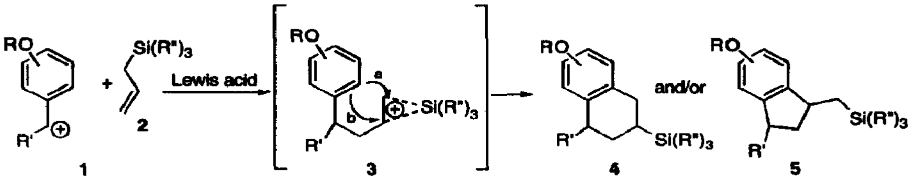
Abstract: Allylsilanes serve as three-carbon dipole equivalents for the formation of tetrahydronaphthalenes *via* Lewis-acid promoted formal [3+3]-cycloadditions with benzylic cations. A competing [3+2]-pathway resulted in the formation of dihydro(1*H*)indenes. Both quinone methides and benzylic alcohols were used as precursors to the benzylic cations.

Allylsilanes have seen wide application as allylic anion equivalents in reactions with various types of electrophiles.[1] Recently, several groups have shown allylsilanes to be efficient three-carbon cycloaddends in formal [3+2]-cycloadditions with α,β-unsaturated carbonyl compounds[2-4] and nitrosium salts.[5] In these reactions, the silicon atom, which serves to stabilize the adjacent positive charge, undergoes a 1,2-migration and is retained in the final product. A mechanistically related reaction using allenylsilanes was previously reported by Danheiser and coworkers.[6] We have shown that benzylic cations can serve as three-carbon cycloaddends in formal [3+2]-cycloaddition reactions with alkenes,[7] and [3+3]-cycloadditions with allenylsilanes[8] and considered exploring similar methodology with allylsilanes.

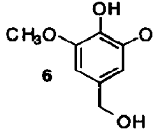
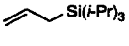
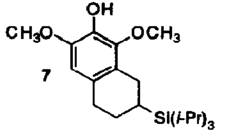
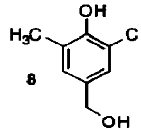
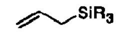
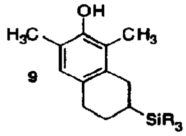
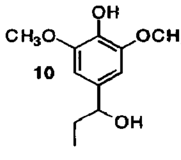
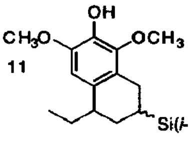
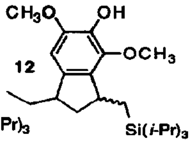
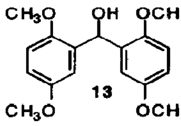
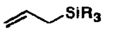
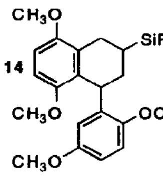
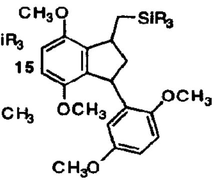
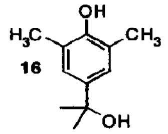
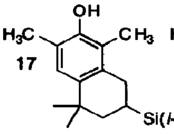
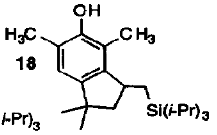
The use of allylsilanes in formal cycloadditions with benzylic cations may allow the preparation of tetrahydronaphthalenes *via* a formal [3+3]-cycloaddition (Scheme 1). Initially, it was not clear if the intermediate silyl stabilized cation, **3**, would undergo silyl migration to form a tetrahydronaphthalene (**4**, path *a*), or a dihydro(1*H*)indene (**5**, path *b*). We report here our initial observations on this reaction and the factors affecting the formation of tetrahydronaphthalene and dihydro(1*H*)indene products.[9]

Scheme 1. Proposed Formal [3+3]- and [3+2]-Cycloaddition Reaction.



Allyltriisopropylsilane and allyl*tert*-butyldiphenylsilane were chosen for this initial study because Danheiser[6d] had shown that increased steric bulk at silicon suppresses loss of silicon.[10,11] Table 1 summarizes our results using benzylic alcohols as the benzylic cation precursor. The presence of an acid scavenger, methyltrimethoxysilane or di-*tert*-butylpyridine, and an excess of allylsilane were required for good yields of products.[12] Primary benzylic cations afforded good yields of tetrahydronaphthalenes with no trace of dihydro(1*H*)indenes, irrespective of which allylsilane was used (entries 1-3). Secondary benzylic cations, however, afforded mixtures of five- and six-membered ring products (entries 4-6). It is interesting to note that bis-benzylic alcohol **13** afforded **14** and **15** as single diastereomers (capillary GC, ^1H NMR analysis). Tertiary benzylic alcohol **16** (entry 7) afforded a low yield of both five- and six-membered ring products. A preliminary survey of benzylic alcohols lacking substituents on the aryl ring showed polymerization of the benzylic alcohol to be the major reaction pathway.

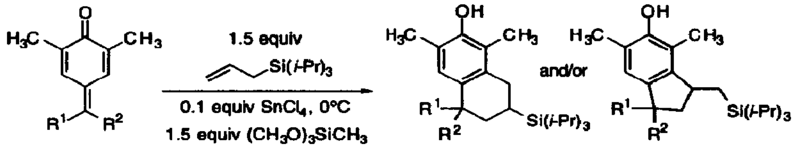
Table 1. Reactions of Benzylic Alcohols with Allylsilanes.[a]

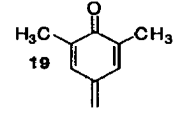
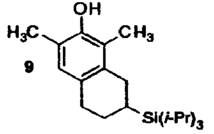
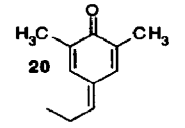
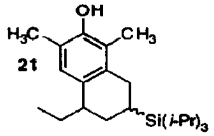
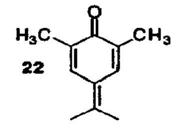
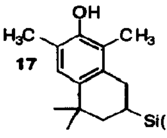
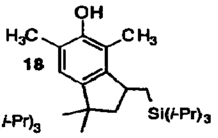
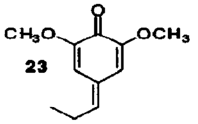
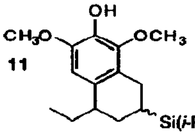
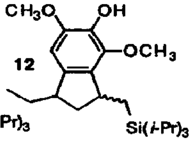
Entry	Starting Material	Conds[a]	Allyl Silane	Product(s)	Yield(%)
1	 **6**	B		 **7**	51
2	 **8**	B	 R_3 = $(Ph)_2t$-Bu	 **9**	64
3		A	R_3 = $(i$-$Pr_3)$		71
4	 **10**	A		 **11** 27% (1 : 1)[d]  **12** 53% (4.7 : 1)[d]	80[b]
5	 **13**	B	 R_3 = $(Ph)_2t$-Bu	 **14**  **15**	87 **14** : **15** (0 : 1)[c]
6		B	R_3 = $(i$-$Pr_3)$		90[e] **14**[f] : **15**[f] (2 : 5)
7	 **16**	A		 **17**  **18**	35[e] **17** : **18** (3 : 2)

[a]General Procedure: $SnCl_4$ (3 equiv, 1.0 M in CH_2Cl_2) was added to a solution of the benzylic alcohol (1 equiv), acid scavenger (10 equiv; conditions A = $CH_3Si(OCH_3)_3$; B = 2,6-di-*t*-butylpyridine), and allylsilane (5 equiv) in CH_2Cl_2 (0.02 M in benzylic alcohol) at 0°C. After 30 min, aqueous workup ($NaHCO_3$) and flash chromatography afforded the product(s) in the yields indicated. [b]HPLC separation afforded the products in the yields shown. [c]Ratio of isomers by ^1H NMR. [d]Inseparable mixture, ratio determined by GC. [e]Reported yield is for the mixture of isomers; HPLC separation afforded each isomer for characterization. [f]Single diastereomer by GC analysis.

Quinone methides could also be used as precursors to the benzylic cations (Table 2).[13] Entries 1, 3, and 4 in Table 2 gave the same products as entries 2, 7, and 4 in Table 1, respectively. In these cases the yields and ratios of five- *vs.* six-membered ring products were similar, showing the reactions to be independent of cation precursor. A major advantage offered by a quinone methide route to a benzylic cation is that a catalytic amount of Lewis acid (0.1 equiv.) may be employed.

Table 2. Reactions of Quinone Methides with an Allylsilane.



Entry	Quinone Methide	Product(s)	Yield(%)
1	**19** 	**9** 	78
2	**20** 	**21** 	76 (3:1)^{a}
3	**22** 	**17**  **18** 	34^{b} **17** : **18** (3 : 2)
4	**23** 	**11**  **12**  (1.6 : 1)^{a,c} (2.7 : 1)^{a,c}	49 **11** : **12** (1 : 1)

[a] Ratio of diastereomers by GC. [b] HPLC separation afforded the products in the yields shown. [c] Inseparable mixture.

There appear to be at least three factors that affect the ratio of tetrahydronaphthalene to dihydro(1*H*)indene products: (1) substituents on silicon; (2) substituents on the aryl ring of the benzylic cation; and (3) substitution on the benzylic carbon of the cation.[14] Primary benzylic cations afforded tetrahydronaphthalene products, regardless of substitution on the benzylic cation or on silicon. Secondary and tertiary benzylic cations afforded tetrahydronaphthalene and/or dihydro(1*H*)indene products depending on the factors noted above. For example, the cations derived from **20** (Table 2, entry 2) and **23** (Table 2, entry 4) are both secondary benzylic cations. Quinone methide **20** afforded six-membered ring cyclization product **21** exclusively, whereas **23** afforded a mixture of both five- and six-membered ring products (**11** and **12**). The formation of dihydro(1*H*)indene **12** from **23** can be attributed to the difference in substitution on the aryl ring of the benzylic cation; the aryl ring of the intermediate β-silylcation derived from **23** is activated toward electrophilic aromatic substitution relative to that derived from **20**. Treatment of bis-benzylic alcohol **13** with allyltriisopropylsilane afforded a mixture of five- and six-membered ring products (Table 1, entry 6). The more bulky allyl*tert*-butyldiphenylsilane afforded dihydro(1*H*)indene **15**; R_3 = *t*-Bu(Ph$_2$) exclusively (Table 1, entry 5). The complete selectivity for the five-membered ring closure is noteworthy. It may be that the changes in ratio of the dihydro(1*H*)indenes to the tetrahydronaphthalenes are due to a difference in the degree of vertical *vs.* bridging stabilization of the intermediate β-silylcations. Rapid capture of the intermediate silyl-stabilized cation, prior to bridging, would afford a larger portion of dihydro(1*H*)indene.[10,11] Tertiary benzylic cations also afforded dihydro(1*H*)indene products. This may be due to a *gem*-dialkyl effect.[15]

The results of this study show that both formal [3+3]- and [3+2]-cycloadditions are possible with allylsilanes and benzylic cations. An in-depth study of these competing formal cycloadditions may allow the factors affecting silyl migration to be examined. We are currently exploring the regio- and stereoselectivity of this reaction with substituted allylsilanes and will report the results in due course.

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9. In our allenylsilane work, spirodecadienone products were observed.[8] No spirodecadienone, or allylation products, were observed in the allylsilane formal cycloadditions reported here.
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12. Initial optimization of the reaction conditions led to the use of 5 equiv. of allylsilane. The influence of the equivalents of allylsilane employed on the yield of the reaction will be described in a full paper.
13. For leading references on the chemistry and synthesis of quinone methides see reference 5 and: Angle, S. R.; Turnbull, K. D. *J. Am. Chem. Soc.* **1989**, *111*, 1136-1138.
14. To test the stability of the products to the reaction conditions three control reactions were carried out: a mixture of **14** and **15**, pure **14**, and pure **15** were resubjected to the reaction conditions. There was no change in any of the three reactions by GC analysis.
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