SYNTHESIS OF 1,2-DIHYDRONAPHTHALENES AND SPIRO[4.5]-DECA-3,6,9-TRIEN-8-ONES FROM BENZYLIC ALCOHOLS

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Abstract: The synthesis of 1,2-dihydronaphthalenes and spiro[4.5]decatrienones via reaction of an allenylsilane and a benzylic cation is reported.

Dihydronaphthalenes are important synthetic intermediates that have served in anthracyclinone synthesis¹ and can undergo bromination,² cyclopropanation,³ dipolar cycloaddition⁴ and epoxidation⁵ reactions to afford useful products. A recent report from our laboratory described a formal 3 + 2 cycloaddition of quinone methides with alkenes to give dihydo-1H-indenes.⁶ We sought to extend this methodology to the formation of six-membered carbocycles utilizing allenylsilanes in a formal 3+3 cycloaddition.⁷ Danheiser and co-workers have used allenylsilanes as a three-carbon building block to form five-, six- and seven-membered ring systems.^{8,9} For example, treatment of allenylsilane 2 with tropyllium cation 1 afforded azulene 3 in good yields (equation 1).⁹



The general strategy (equation 2), calls for formation of a benzylic cation from benzylic alcohol 4, followed by reaction with allenylsilane 5 to afford vinyl cation 8, which is expected to undergo silyl migration to afford a second vinyl cation, $9.^{8,9}$ Intermediate 9 should be captured to afford a fused ring product 6 if R¹ \neq OH.¹⁰ If R¹ = OH, *ipso*-attack on cation 9 is expected to result in the formation of spiro[4.5]decatrienone 7.^{11a} Thus, the synthesis of either dihydronaphthalenes 6 and/or spiro[4.5]decatrienones 7 might be possible via this approach.^{10,11} The spiro[4.5]decatrienone products 7 are highly functionalized and might serve as key intermediates in the synthesis of sesquiterpenes possessing this skeleton (e. g. spirovetivanes, acorones and alaskanes).¹²

The benzylic alcohols required for this study were either commercially available or prepared from the corresponding benzaldehydes.¹³ The allenylsilanes were prepared from propargylic alcohols using the general procedure of MacDonald and Reagan.¹⁴ Our results are summarized in Table 1.

The best yields of products were obtained when either the allenylsilane or the benzylic alcohol was used in excess. Optimal conditions using excess allenylsilane employ it in an approximate 10:1 molar ratio relative to benzylic alcohol (entries 1, 3, 5, 8). For example, treating alcohol **23** with 19.6 equivalents of allenylsilane **21** and 2.0 equivalents of tin (IV) chloride in the presence of methyltrimethoxysilane (acid





scavenger, 7.0 equiv, CH_2Cl_2 , 0 °C) afforded dihydronaphthalene 24 in 65% yield (entry 8). As the number of equivalents of allenylsilane was reduced to 4.3, then to 2.1 and finally to 1.4, the yield decreased to 39%, 16% and 14% respectively (entries 9-11). The reaction can also be carried out using an excess of benzylic alcohol. For example, treating 2.0 equivalents of alcohol 10 with allene 11 afforded dihydronaphthalene 12^{15} in 79% yield (entry 2). Obviously, the use of an excess of one of the reactants is a drawback. However, both of the reactants are readily available and either can be used in excess.

Benzylic alcohols lacking a *para*-hydroxyl group, (**18** and **20**), can only afford dihydronaphthalene products. However, even when the benzylic alcohol has a *para*-hydroxyl group, the presence of two adjacent methoxy groups (**10** and **23**) results in the exclusive formation of dihydronaphthalene products (entries **1** and **8**). Alcohol **13** has a single methoxy group adjacent to the phenol and affords a 1:1 mixture of dihydronaphthalene **14** and spirodienone **15** (entry **3**). Phenol **16** lacks activating substituents *ortho* to the phenol and affords spirodienone **17** as the exclusive product (entry **4**).

It is possible that the formation of dihydronaphthalenes proceeds through the initial formation of the spirodienone, followed by dienone-phenol rearrangement.¹⁶ This possibility was tested by resubmitting spirodienone **15** to the reaction conditions. Unreacted spirodienone **15** was recovered. This experiment does not support the intermediacy of spirodienones, instead the results can be rationalized as a competition between *ipso*-attack to afford the spirodienone and electrophilic aromatic substitution to afford the dihydronaphthalene. This explanation is consistent with dimethoxy phenols **10** and **23** affording only dihydronaphthalene products. Two methoxy groups (*ortho* and *para* to the site of nucleophilic attack) facilitate the electrophilic aromatic substitution. Mono-methoxy phenol **13**, with only a single methoxy group to assist the electrophilic aromatic substitution, affords a mixture of spiro and fused products. Phenol **16** with no substituents to facilitate the electrophilic aromatic substitution, affords only spiro product **17**.

Alcohol 18 which lacks a *p*-substituent capable of stabilizing a benzylic cation also underwent formal cycloaddition to afford dihydronaphthalene 19 in good yield (entry 5). The lower yield (44%) in entry 7, is not surprising when one considers that even though the methoxy group can stabilize the initial benzylic cation, it can only hinder the subsequent electrophilic aromatic substitution since it is *meta* to to the site of attack.¹⁷

We have shown that, benzylic cations with a wide range of substitution patterns can be used in the reaction and afford adducts in good yields. Substitution on the aromatic ring controls whether dihydronaph-

thalene or spirodecatrienone products are formed. Further studies on the scope and mechanism of the reaction, as well as application of this methodology to the synthesis of natural products are in progress.

Entry	Alcohol	(equiv)	Allene	(equiv)	Product(s)	Yield(%)
1	он он	(1.0)		Bu)Me ₂ (9.7)		65
2		(2.0)	1 1	(1.0)	H ₃ CO 1 2 Et	79
3	1 3 Et OH	(1.0)		(9.9)	HO HO H ₃ CO H_3 CO H_3 CO H_3 CO H_3 CO H_3 CO H_3 CO H_2 CO H_3 CO H_2 CO H_3 CO H_2	8 3 ^b
4		(1.0)		(9.9)	O = Si(<i>t</i> -Bu)Me ₂ 1 7 Et	76
5		(1.0)		(9.4)	Si(t-Bu)Me ₂	77
6		(2.0)		(1.0)	1 9 Et	35
7	2 0 OH	(1.0) PHCH ₂ Ci	Si(<i>t</i> 1 ₂ H 2 1	•Bu)Me ₂ (3.9)	H ₃ CO CH ₂ CH ₂ Ph 2 2	44
8	он н,со, ⊥_осн,	(1.0)		(19.6)	H₃CO HO、↓ ↓ SI(f-Bu)Me₂	65
9	A	(1.0)		(4.3)	H-CO CH-CH-Ph	39
10	2 3 OH	(1.0)		(2.1)	2 4	16
11		(1.0)		(1.4)		14

Table 1. Reaction of Benzylic Alcohols with Allenylsilanes^a

^aAll yields refer to isolated, purified products, characterized by ¹H NMR, ¹³C NMR, IR, MS and HRMS. General Procedure: SnCl₄ (2 equiv) was added to a solution of benzylic alcohol, CH₃Si(OCH₃)₃ (7 equiv) and CH₂Cl₂ (0.02 M in limiting reagent, except for entries 7 and 9 which were 0.08 M) at 0 °C. After stirring 15-30 min aqueous workup (NaHCO₃) and flash chromatography afforded the products in the yields indicated. ^bBoth 14 and 15 are formed; 15 appears to be a single diastereomer by ¹H NMR, ¹³C NMR and HPLC.

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