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# Bis(fluorosulfuryl)imide: a Brönsted Acid Catalyst for the Coupling of Allylic and Benzylic Alcohols With Allyltrimethylsilane

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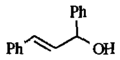
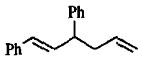
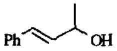
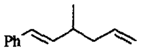
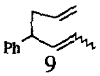
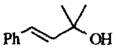
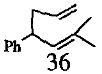
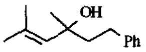
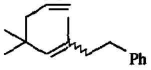
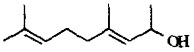
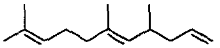
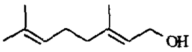
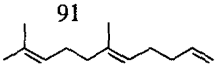
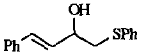
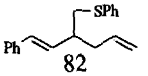
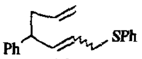
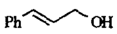
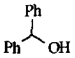
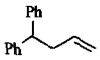
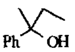
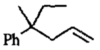
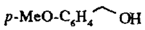
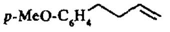
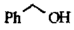
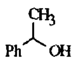
*Abstract* : The Brönsted acid $HN(SO_2F)_2$ catalyses the reaction of allylic and benzylic alcohols with allyltrimethylsilane to give the corresponding coupled products in good yields.

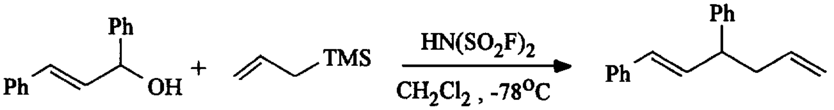
The coupling of two allylic moieties is an important reaction for the synthesis of 1,5-dienes.[1] One common method involves reaction of various derivatives of allylic alcohols such as halides, acetates, ethers and trimethylsilyl ethers with allylsilanes in the presence of various Lewis acids.[2] Allylsilane terminated cation olefin cyclisation of tertiary alcohols catalysed by trifluoroacetic acid (TFA) has also been reported.[3] Similarly, intermolecular coupling of benzylic alcohols[4] or its ethers[2b] is also known to occur in the presence of Lewis acids. However there has been no report in the literature where this type of coupling has been reported using allylic alcohols as such for the synthesis of 1,5-dienes. Any method which uses these alcohols is highly desirable because it would avoid an additional step of conversion of these alcohols to their corresponding halides, acetate or ethers. Recently we found that allyltrimethylsilane is stable in the presence of Brönsted acid bis(fluorosulfuryl)imide [$HN(SO_2F)_2$].[5] We reasoned that under these conditions, $HN(SO_2F)_2$ may activate allylic and benzylic alcohols via protonation for reaction with allyltrimethylsilane.

Herein, we wish to report that Brönsted acid $HN(SO_2F)_2$[6] indeed catalyses the coupling of allylic as well as benzylic alcohols with allyltrimethylsilane. A solution of 1,3-diphenylpropenol (1.0 equiv) **1** in $CH_2Cl_2$ was slowly added over a period of 15-20 min to a mixture of allyltrimethylsilane (1.5 equiv) and 10 mol% of $HN(SO_2F)_2$ at -78°C. The reaction was complete in under 5 min after the addition as indicated by TLC. After usual aqueous work up product **2** was obtained in 82% yield. When instead of alcohol **1**, diphenylcarbinol **3** was used, the corresponding coupled product **4** was obtained in 96% yield.[7] When the first reaction was carried out in the presence of 5 fold excess of 2,6-di-*tert*-butyl-4-methyl pyridine, a known proton scavenger,[5,8] with respect to $HN(SO_2F)_2$, it did not give the desired product. This experiment suggested that the coupling reaction is indeed catalysed by $HN(SO_2F)_2$.

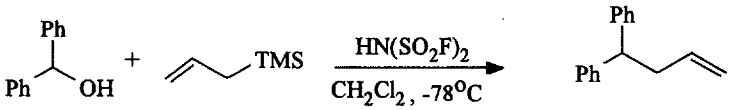
**Table 1 : Reaction of allyltrimethylsilane with various allylic and benzylic alcohols in the presence of HN($SO_2F_2$)$^a$ (10 mol %).**

| Entry | Substrate | t/min. | Product (α : γ ratio)$^b$. | | Yield (%) |
|---|---|---|---|---|---|
| 1. |  | 5 |  | | 82 |
| 2. |  | 5 | <br>91 | <br>9 | 92 |
| 3. |  | 5 | <br>64 | <br>36 | 71 |
| 4. |  | 10 | <br>46 | <br>54 | 55 |
| 5. |  | 30 | <br>91 | <br>9 | 48 |
| $^c$6. |  | 30 |  | | 15 |
| $^d$7. |  | 120 | <br>82 | <br>18 | 82 |
| 8. |  | | No Reaction | | |
| 9. |  | 5 |  | | 96 |
| 10. |  | 10 |  | | 78 |
| 11. |  | 5 |  | | 90 |
| 12. |  | | No Reaction | | |
| 13. |  | | No Reaction | | |

$^a$All reactions were carried out in 4 $cm^3$ $CH_2Cl_2$/mmol of alcoholic compound at -78°C under $N_2$ atmosphere. $^b$Determined by $^1$HNMR. $^c$The yield was determined from crude NMR and only one isomer was observed. $^d$The reaction was carried out at 0°C.



Eq.1

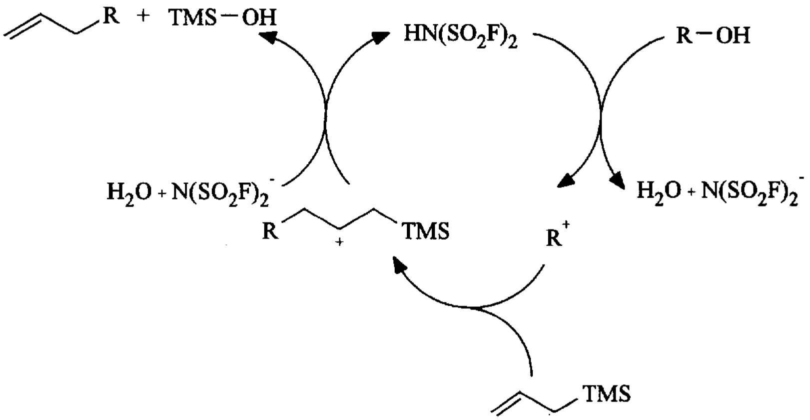


Eq.2

After establishing that $HN(SO_2F)_2$ is the actual catalyst involved, the reactions using various allylic and benzylic alcohols were studied. The results are summarized in Table 1. Most of the alcohols smoothly underwent allylation. Primary alcohols like benzyl alcohol and cinnamyl alcohol did not give the desired product. The former alcohol was recovered as such but the latter alcohol gave only polymeric material. Geraniol gave the product in low yield. 1-Phenethyl alcohol was unreactive under these conditions. The presence of a thiophenyl group at the ß-position considerably slowed down the reaction (Table 1, entry 7); this may be due to the stability of the carbocation intermediate as an episulfonium ion, thus making it less reactive.[2c,9] 1-Methylgeraniol gave the desired product in moderate yield (48%) and the rest of the product obtained appears to be derived from intramolecular cyclisation.

The most probable catalytic cycle involved is shown in scheme 1. The Brönsted acid generates a carbocation which is trapped by allylsilane to give the silicon stabilised carbocation. The water molecule being more nucleophilic than $N(SO_2F)_2^-$ removes the TMS group to give the product and the catalyst is regenerated.

**Scheme 1**



In conclusion, the work demonstrates the coupling of allylic and benzylic alcohols with allyltrimethylsilane catalysed by a Brönsted acid $HN(SO_2F)_2$. Only 10 mol% of catalyst is sufficient to accomplish the coupling.

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6. (a) Ruff, J.K. *Inorganic Chem.* **1965**, *4*, 1446; (b) Ruff, J.K. and Lustig, M. *Inorg. Synth.* **1968,** *11*, 138.
7. When diphenyl carbinol was treated with allyltrimethylsilane in the presence of 25 mol% of TFA no coupled product was obtained even at room temp. after 10h and starting material was recovered. However, when 1,3 diphenyl propenol was used instead of diphenyl carbinol about 7% of the coupled product was obtained at room temp. after 10h. These results clearly indicate that $HN(SO_2F)_2$ is much superior as a catalyst for this type of coupling reactions than the commonly used Brönsted acid TFA for cation olefin cyclization initiated by tertiary alcohols.
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