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FULL PAPER

Hexafluoroisopropanol Promoted Metal-Free Allyllation of Silyl Enol Ethers with Allylic Alcohols

Juana M. Pérez,[a] Cristina Maquilón,[a] Diego J. Ramón[a] and Alejandro Baeza[a]*

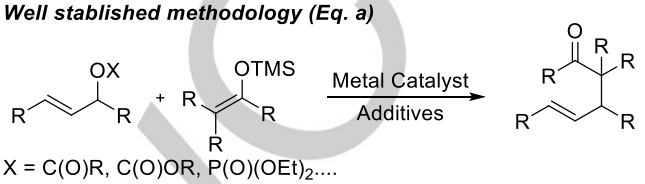
Abstract: A metal-free protocol for the reaction of silyl enol ethers with allylic alcohols based on the use of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) as promoter able to activate both reactants, is herein described. This simple and straightforward transformation proceeds under smooth conditions rendering the corresponding allylated products generally in good yields.

Introduction

The allylic substitution reaction is a widespread and powerful methodology which allows organic chemists the introduction of an endless number of nucleophiles at the allylic position of a molecule.[1] Among such myriad of nucleophiles employed in this reaction, silyl enol ethers can be considered as challenging ones, since their use implies the combination of metal catalyst, which is the responsible for the electrophilic π-allyl intermediate formation and, in most of the cases, a promoter able to activate the silyl enol ether. In addition, this apparently simple transformation becomes even more complicated since both processes must be somehow synchronized, because a fast hydrolysis of the silyl enol ether towards its keto form could deactivate the nucleophile, then leading to the reaction failure. In this regard, and despite the mentioned drawbacks, several groups have been able to carry out this transformation in a transition metal-catalyzed reaction onto alcohol derivatives, such as carbonates, phosphates, acetates…, being in some cases, necessary the use of a silyl enol ether activator (Scheme 1, eq. a).[2] The use of allylic alcohols in this transformation is less common. This strategy not only reduce the waste formed in the reaction but also avoid a previous manipulation of the allylic substrate to convert the hydroxyl into a good leaving group.[3] In fact, as far as we know, there are only a couple of examples in the literature, being both catalyzed by an iridium complex (Scheme 1, eq. b).[4]

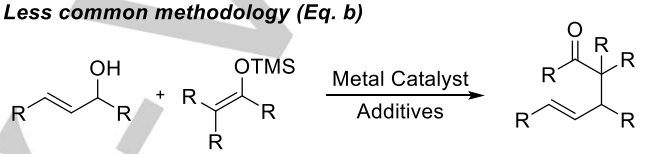
With these precedents in mind we decided to explore the possibility of performing this transformation using allylic alcohols in a metal-free transformation (Scheme 1, eq. c). In this sense, in order to tackle this synthetic challenge, we envisioned fluoroalkyl alcohols as promising solvent candidates to accomplish the purpose not only due to their unique chemical and physical properties (such as a high hydrogen bond donor ability, low nucleophilicity, high polarity and ionizing power values and a slight Brønsted acidity)[5] but also because they have shown both, to be able to promote the nucleophilic substitution reaction onto the so-called π–activated alcohols[6,7] and activate silicon-based nucleophiles.[8] The results of this study are herein presented.

Well stablished methodology (Eq. a)

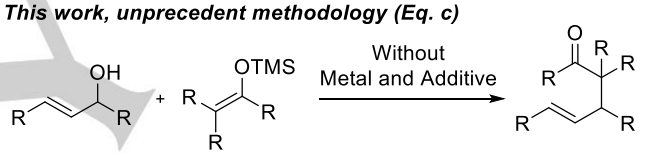


X = C(O)R, C(O)OR, P(O)(OEt)$_2$....

Less common methodology (Eq. b)



This work, unprecedent methodology (Eq. c)



Scheme 1. Different allylation strategies employing silyl enol ethers.

Results and Discussion

We initiated our study by choosing the reaction between (*E*)-1,3-diphenylprop-2-en-1-ol (**1a**) and silyl enol ether **2a** (2 equiv.) as a model reaction in order to find the optimal conditions (Table 1). Firstly, 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) was essayed at 50 ºC, and to our delight a 70% conversion towards the allylation product **3aa** was observed (Table 1, entry 1). By increasing the amount of nucleophile (until 2.5 equivalents) we were able to raise the conversion up to 86% (Table 1, entry 2). The amount of HFIP seems to play an important role, since reducing the volume to the half resulted in a considerable drop in the conversion (Table 1, entry 3). It is worth to remark that after the reaction time no unreacted allylic alcohol remained, being the corresponding fluorinated ether (**4**) the main by-product observed. Next, 2,2,2-trifluoroethanol (TFE) which possesses lower hydrogen bond ability, polarity, ionizing power and Brønsted acidity along with higher nucleophilicity, in comparison with HFIP, was tested. However, lower conversions of **3aa** were observed even when temperature was increased up to 70 ºC. In this case, the 2,2,2-trifluoroethyl ether derivative (**5**) was the main product obtained (Table 1, entries 4 and 5). When water, which also has a high polarity and hydrogen bond ability, was used as solvent, the dimerization product of **1a** (**6**) was the main product observed (Table 1, entry 6). Other non-fluorinated alcohols, such as ethanol,

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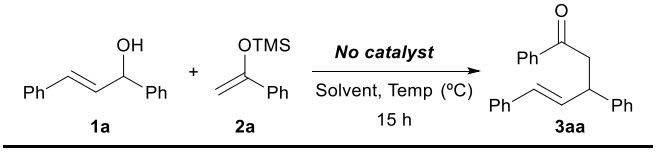
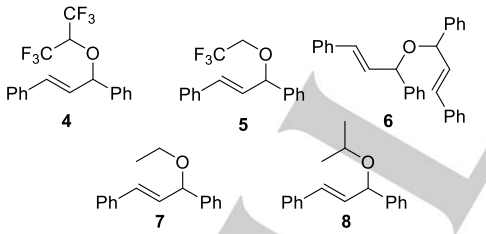
led to the formation of ethoxy-derivative (**7**) as major product due to the higher nucleophilicity of this solvent (Table 1, entry 7). To check whether the presence of fluorine atoms in the solvent structure was a key issue for the reaction to proceed, either perflurohexane or a 1/1 mixture of perfluorohexane and isopropanol were also evaluated. However, the corresponding dimerization product of **1a** (**6**) and the allylic isopropyl ether **8** were the main compounds detected (Table 1, entries 8 and 9)

Table 1. Optimization of the reaction conditions[a]



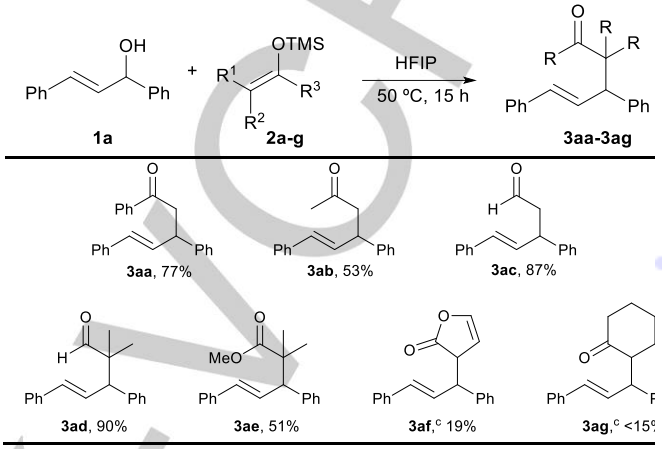
Entry	Solvent	Temp (º C)	Conv. (%)[b]
1	HFIP	50	70
2	***HFIP***	***50***[c]	***86***
3	HFIP[d]	50[c]	72
4	TFE	50[c]	27
5	TFE	70[c]	45
6	H_2O	50[c]	32
7	EtOH	50[c]	11
8	C_6F_{14}	50[c]	<10
9	C_6F_{14}/^{i}PrOH (1/1)	50[c]	<5

[a] Reaction conditions: alcohol **1** (0.25 mmol), **2a** (2 eq.) in the appropriate solvent (250 µL, 1M of **1**). [b] Conversion to **3aa**, determined by GC. [c] 2.5 eq. of **2a** were used. [d] 125 µL of HFIP (2M of **1**) were used.



Once the optimal reaction conditions (Table 1, entry 2) were selected, we next focused our attention to evaluate the performance of others silyl enol ethers (Table 2). Thus, as mentioned above, the reaction of alcohol **1a** with enol ether **2a** rendered the corresponding ketone **3aa** in good yield. When **2b** (R^1 = R^2= H, R^3 = CH_3) was employed only moderate yield was achieved for **3ab**. However, we were pleased to obtain aldehyde **3ac** in excellent yield when acetaldehyde-derived trimethylsilyl enol ether was used (R^1 = R^2= R^3 = H). Similarly, aldehyde **3ad** was obtained in high yield using isobutyraldehyde-derived enol ether (R^1 = R^2= CH_3, R^3 = H). Next, compound **2e** (R^1 = R^2= H, R^3 =OCH_3) was evaluated affording ester **3ae** in moderate yields. Unfortunately, when cyclic silyl enol ethers, such as furan- and cyclohexyl-derived (**2f** and **2g**, respectively) ones, were assayed low yields were obtained.

Table 2. Silyl enol ethers scope [a]

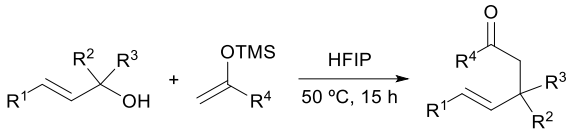


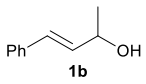
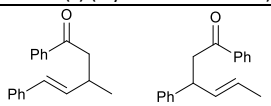
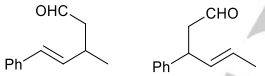
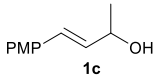
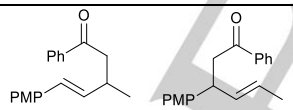
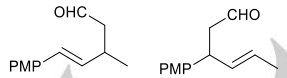
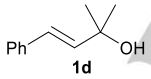
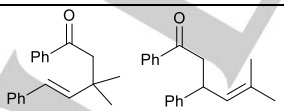
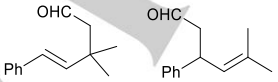
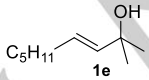
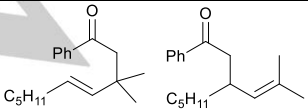
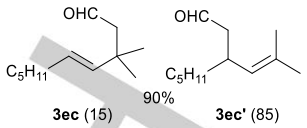
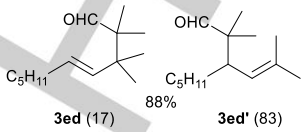
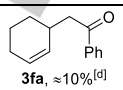
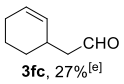
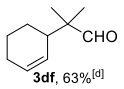
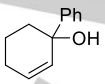
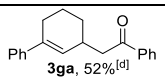
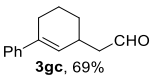
[a] Reaction conditions: alcohol **1a** (0.25 mmol), **2** (2.5 eq.) in HFIP (250 µL, 1M of **1a**). [b] Isolated yields after flash chromatography. [c] Not isolated, yield calculated by ^{1}H NMR.

Next, in order to evaluate the scope and limitations of this methodology, other allylic lineal non-symmetric alcohols were submitted to the optimal reaction conditions using silyl enol ethers **2a** and **2c** (Table 3). In all the cases a regioisomeric mixture of products were obtained.[9,10] Firstly, alcohol **1b**, which would form a quite reactive carbocationic specie (in comparison with that obtained with alcohol **1a**), was submitted to the optimal reaction condition using such enol ethers. Thus, when acetophenone-derived enol ether was tested, low conversion towards product **3ba** was achieved. On the contrary, we were pleased to observe the formation of the product **3bc** in good yield (Table 3, entries 1 and 2) when acetaldehyde derivative **2c** was used. A different behavior was observed when alcohol **1c**, possessing an electron-donating MeO group at the phenyl ring, which could stabilize more effectively the transient carbocationic intermediate, was employed. In this case, as somehow expected, better yields were achieved in both products **3ca** and **3cc** (Table 3, entries 3 and 4). The use of tertiary alcohol **1d**, that would render a more substituted allylic carbocation, produced similar results in terms of both yield and regiochemistry (Table 3, entries 5 and 6). Encouraged by the good results observed with tertiary alcohols, we decided to evaluate non-aromatic alcohol **1e**. To our delight, the corresponding products were obtained in good to high yields. (Table 3, entries 7 and 8). In addition, the more sterically crowded enol ether **2d** was also successfully allylated using this alcohol (Table 3, entries 9). Primary alcohols such as cinnamyl alcohol were also tested but as expected failed to react with enol ether **2a** and only a low conversion towards the desired product was observed with **2c** (along with some unidentified products).[11,12] Finally, cyclic allylic alcohols were taken into account. As previously observed for the lineal alcohols, the reaction between secondary cyclohexenyl derived alcohol **1f** and **2a** did not

afforded the desired product but the corresponding fluorinated ether (Table 3, entry 10). On the other hand, when **2c** was employed almost a total consumption of the alcohol was observed. However, in this case, along with small amounts of fluorinated ether, the expected product was detected by GC-MS among a complex mixture of different products (most of them aldehydes coming from product **3fc** aldol auto-condensation) (Table 3, entry 11). To avoid such myriad of compounds, the bulkier dimethyl substituted enol ether **2d** was employed, obtaining a 63% yield of the corresponding product **3fd** (Table 3, entry 16). Finally, as expected, better results were observed when tertiary cyclic alcohol **1g** was studied. In both cases, the product with the isomerized double bond was obtained as sole regioisomer with modest to good yields (Table 3, entry 13 and 14).[9,10]

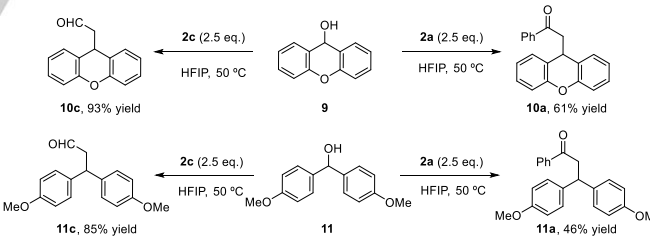
Table 3. Allylic alcohols scope[a]



Entry	Alcohol	2	Product(s) (%yield[b] and ratio[c])
1	 **1b**	**2a**	 **3ba** ≈15%[d] **3ba'**
2		**2c**	 **3bc** (60) 80% **3bc'** (40)
3	 **1c**	**2a**	 **3ca** (30) 67% **3ca'** (70)
4		**2c**	 **3cc** (40) 91% **3cc'** (60)
5	 **1d**	**2a**	 **3da** (20) 54% **3da'** (80)
6		**2c**	 **3dc** (25) 87% **3dc'** (75)
7	 **1e**	**2a**	 **3ea** (35) 53% **3ea'** (65)
8		**2c**	 **3ec** (15) 90% **3ec'** (85)
9		**2d**	 **3ed** (17) 88% **3ed'** (83)
10	 **1f**	**2a**	 **3fa**, ≈10%[d]
11		**2c**	 **3fc**, 27%[e]
12		**2d**	 **3df**, 63%[d]
13	 **1g**	**2a**	 **3ga**, 52%[d]
14		**2c**	 **3gc**, 69%

[a] Reaction conditions: alcohol **1** (0.25 mmol), **2** (2.5 eq.) in HFIP (250 µL, 1M of **1**) at 50 ºC. [b] Isolated yields after flash chromatography. [c] Determined by ^{1}H NMR and GC from the crude reaction. [d] Not isolated, yield calculated by ^{1}H NMR. [e] Not isolated, detected by GC-MS.

To further extend this new methodology, activated benzylic alcohols were also evaluated under the optimized reaction conditions (Scheme 2).[13] Xanthydrol (**9**) was firstly evaluated and produced the desired ketone and aldehyde in good and excellent yield, respectively. When a more hindered alcohol, as bis(4-methoxyphenyl)methanol (**11**), was used lower yields were obtained for the alkylation products **11a** and **11c**, as expected.



Scheme 2. Alkylation of silyl enol ethers using benzylic alcohols.

In view of the obtained results, we decided to investigate the reasons behind the better performance of the reactions in which aldehyde-derived silyl enol ethers are involved. For such purpose, some mechanistic probes were performed. In this regard, allylic alcohol **1a** was allowed to react under optimized conditions with acetophenone and acetaldehyde, respectively (Scheme 3, Eq. A). As can be observed, whereas the former did not react at all, the latter produced the corresponding allylation product in a modest 40% conversion. This observation prompted us to perform a kinetic study of the model reaction and it was monitored by GC-

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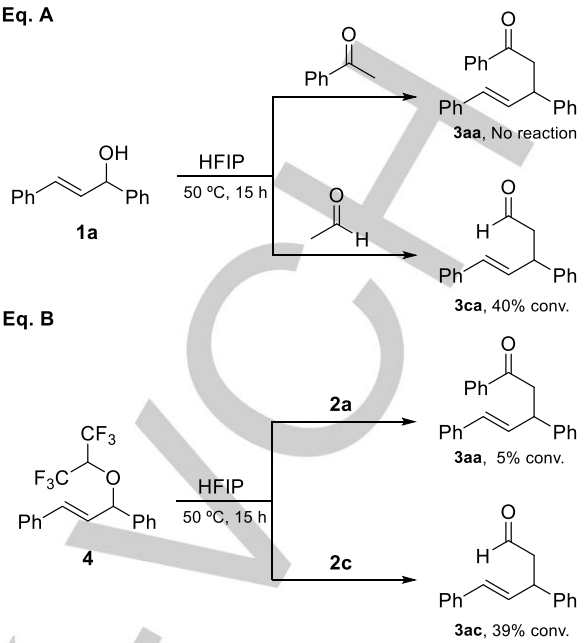
MS. Surprisingly, we realized that both alcohol **1a** and enol ether **2a** reacted in less than 1 hour giving the corresponding product **3aa**, fluorinated ether **4**, and acetophenone, respectively, reaching the maximum conversion towards **3aa** and remaining constant after this time. Additionally, and since fluorinated ether **4** is formed (even at the early stages of the reaction) we decided to synthesize such compound and evaluate their ability as allylating agent (Scheme 3, Eq. B). As depicted, the reaction with **2a** barely worked, and again a modest yield was observed with aldehyde-derived silyl enol ether **2c**. With all these data in hands and assuming a S_N1-type mechanism, we could visualize two different pathways depending on the enol ether employed. Apparently, when using ketone derivative **2a** the reaction occurs directly through a "naked" carbocation, which could be stabilized by HFIP.[14] The hydrolysis of such enol ether, promoted by HFIP, seems to be pretty fast and when it takes place, no other process is occurring. On the contrary, the employment of aldehyde derivative **2c** seems to imply different simultaneous processes. Thus, in addition to the main direct S_N1-type reaction other pathways can be added, such as the reaction of **2c** with **4**, and the reaction of the corresponding aldehyde with **1a** or **4**. The sum of all these different pathways would explain the higher yields obtained using aldehyde-derivatives. In fact, when the reaction of alcohol **1a** with **2c** was monitored by GC-MS, despite the prompt formation of ether **4**, the conversion was constantly growing until its consumption.

Concerning the regiochemistry of the process and in view of the results depicted in Table 3, some conclusions could be drawn. Firstly, from the results obtained with tertiary alcohols **1d**, **1e** and **1g** it looks like the regioselectivity is governed by the double bond stability, hence favoring the formation of the most substituted olefin. On the contrary, with secondary alcohols **1b** and **1c**, which would produce more reactive carbocation, the regiocontrol is lower and apparently kinetically controlled, being slightly superior for the regioisomer in which the nucleophile attacks the more stable carbocationic intermediate.



Scheme 3. Mechanistic study probes.

Conclusions

In summary, herein we have disclosed a straightforward methodology for the allylation of silyl enol ethers employing π-activated alcohols as allylating agents mediated by HFIP under mild conditions. The employment of such alcohols, avoiding the need of a previous pre-activation and producing water as by-product, and the absence of a metal catalyst, could be seen as a greener alternative to the existing protocols. In general, good yields are obtained for the corresponding products, been remarkable the results achieved with aldehydes-derived enol ethers, which have been scarcely employed in this transformation These better yields obtained for the aldehydes could be ascribed to a different reaction pathway in these cases, as it has been demonstrated by means of different mechanistic probes.

Experimental Section

General procedure for the allyllation of silyl enol ethers with allylic alcohols:

In an open-air flask the silyl enol ether **2** (2.5 eq.) was added to a stirred solution of the corresponding alcohol **1** (0.25 mmol) in HFIP (250 µL, 1M of **1**) and the reaction was maintained at 50 ºC during 15 h. After that time, the reaction mixture was evaporated under reduced pressure to remove the solvent. The crude was directly purified by flash chromatography.

For general remarks and physical and spectroscopical analysis of the allylation products see supporting information.

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Keywords: allylic substitution • fluorinated alcohols • silyl enol ethers • S_N1 • metal-free

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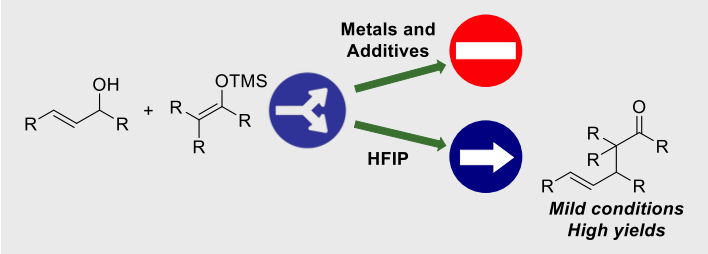

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Hexafluoroisopropanol Promoted Metal-Free Allyllation of Silyl Enol Ethers with Allylic Alcohols