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Direct allylation of benzyl alcohols, diarylmethanols, and triarylmethanols mediated by XtalFluor-E

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ABSTRACT

Article history: Received Received in revised form Accepted Available online We report the direct allylation of benzyl alcohols, diarylmethanols and triarylmethanols mediated by XtalFluor-E using allyltrimethylsilane. The resulting allylated products are obtained in moderate to high yield.

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Keywords: Benzyl alcohols Diarylmethanols Triarylmethanols Allylation Diethylaminodifluorosulfinium tetrafluoroborate

The reagent XtalFluor-E, [(Et₂NSF₂)BF₄], was initially developed as a safer alternative to diethylaminosulfur trifluoride (DAST) and related derivatives for deoxofluorination reactions.¹ Over the years, we² as well as others³ have exploited this reagent as a promoter for a number of transformations. In particular, we have recently reported its use as a stand-alone promoter for the S_N1 reaction of benzyl alcohols using arenes as nucleophiles (Fig. 1).^{2f} In this Friedel-Crafts benzylation, a benzyl alcohol (1; R¹, R² = H) or diarylmethanol (1; R¹ = Ar¹, R² = H) reacts with XtalFluor-E to initially generate an alkoxy-*N*,*N*-diethylaminodifluorosulfane (2).^{1,4} The latter ionizes to generate a benzylic carbocation (3)⁵ that react with the aromatic nucleophile to generate the 1,1-diarylmethane (4; R¹, R² = H) or 1,1,1-triarylmethane (4; R¹ = Ar¹, R² = H).

As a potential extension of this work, we wondered if it would be possible to intercept the carbocationic intermediate **3** with other π -nucleophiles.⁶ Herein, we report that allyltrimethylsilane is a competent nucleophile and its use allows the allylation of benzyl alcohols (**1**; R¹, R² = H), diarylmethanols (**1**; R¹ = Ar¹, R² = H), and triarylmethanols (**1**; R¹ = Ar¹, R² = Ar²) to produce, as shown in Figure 1, allylated products (**5**)^{7,8,9} that are useful, versatile and valuable synthetic intermediates.



Figure 1. Previous and current work.

We initially tested the conditions used for the Friedel-Crafts benzylation^{2f} on 4-phenylbenzyl alcohol (6), replacing the aromatic nucleophile with allyltrimethylsilane to obtain the desired allylated product 7 in 65% yield (Scheme 1). Further optimization (amount of allyltrimethylsilane, ratio of $CH_2Cl_2/HFIP$, and temperature) did not improve the yield, so the conditions shown in Scheme 1 were used for the rest of the study.

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Scheme 1. Initial result.

The allylation of benzyl alcohols was first investigated (Table 1). Under the standard conditions, electron-rich benzyl alcohols provided the desired products (8-10) in moderate to excellent yields (60-87%). However, when using electron-poor benzyl alcohols, much lower yields of the allylated products (11-13) were obtained (26-30%).

Table 1

Allylation of benzyl alcohols with allyltrimethylsilane promoted by XtalFluor-E.



In the case of electron-poor benzyl alcohols (**15**, R = EWG), the corresponding dibenzylether (**17** in Figure 2) was observed as a major side product by NMR analysis of the crude mixture. We hypothesize that for electron-rich benzyl alcohols (i.e., R = EDG), reaction with XtalFluor-E would provide the alkoxy-*N*,*N*-diethylaminodifluorosulfane intermediate **16** that would rapidly ionize to the carbocation **18** (path leading to the desired allylated product). In the case of electron-poor benzyl alcohol (i.e., R = EWG), a slower ionization of intermediate **16** would leave enough time for its reaction with the remaining benzyl alcohol (**15**) to produce **17** via a S_N2 reaction¹⁰ and thus becoming a competitive reaction pathway (Figure 2).



Figure 2. Dibenzylether derivatives (17) as a major side products and proposed mechanism for their formation.

The use of diarylmethanols was next examined as we expected that the addition of a second aryl group would further stabilize the carbocation and thus favour ionization over the undesired reaction of the intermediate with residual starting material. As shown in Table 2, moderate to excellent yield (65-96%) of the corresponding allylated products (**18-33**) could be obtained for a wide range of diarylmethanols. This selection included substrates bearing an electron-rich or an electron-poor aryl substituent. For substrates bearing strong electron withdrawing groups (CF₃, SF₅), slightly more forcing conditions (CH₂Cl₂/HFIP (1:1) at rt, or DCE/HFIP (1:1) at 65 °C) were required.

Table 2

Allylation of diarylmethanols with allyltrimethylsilane promoted by XtalFluor-E.



^a Reaction time was 24 h.

^b The reaction was conducted in DCE/HFIP (1:1) at 65 °C.

^c The solvent was CH₂Cl₂/HFIP (1:1).

Finally, the reaction was examined using triarylmethanols as substrates and the results are shown in Table 3. The desired allylated products (**34-38**) were obtained in moderate to excellent yields (50-91%). Both electron-donating (Me, MeO) and



electron-withdrawing (Cl, CF₃) groups were tolerated on the starting triarylmethanols.

Table 3

Allylation of triarylmethanols with allyltrimethylsilane promoted by XtalFluor-E.



^a The reaction was conducted in DCE/HFIP (1:1) at 65 °C.

^b The reaction was conducted in DCE/HFIP (9:1) at 65 °C.

In terms of the mechanism, since allyltrimethylsilane possess nucleophilic parameters⁶ similar to the ones of the aromatic nucleophiles used in the Friedel-Crafts benzylation of benzyl alcohols and diarylmethanols promoted by XtalFluor-E,^{2f} we hypothesize that both transformations proceed through a similar mechanism as shown in Figure 1.

In summary, we have reported the direct allylation of benzyl alcohols, diarylmethanols and triarylmethanols mediated by XtalFluor-E using allyltrimethylsilane.

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Supplementary Material

Supplementary data associated with this article can be found, in the online version, at ...

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- 10. The formation of di(3-phenylpropyl)ether from the reaction of 3-phenylpropan-1-ol with XtalFluor-E has been reported previously (see ref. 1b) and it was proposed that the ether was formed by the S_N2 attack of the alkoxy-*N*,*N*-diethylaminodifluorosulfane intermediate by the unreacted alcohol. We assume a similar mechanism here, although we cannot exclude a S_N1 pathway.

HIGHLIGHTS

- XtalFluor-E mediates the direct allylation of benzylic alcohols derivatives. •
- Benzyl alcohols, diarymethanols, and triarylmethanols can be used as substrates. •
- A wide range of allylated products can be obtained in moderate to excellent yield. •
- For electron-poor benzyl alcohols, dibenzylethers are observed as major side products. •

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