SYNLETT
Spotlight 390

Boron Trifluoride Etherate

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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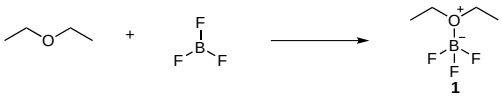
Introduction

Boron trifluoride etherate ($BF_3{\cdot}OEt_2$, **1**) is an effective reagent widely used for a variety of organic transformations,[1] especially for the construction of heterocycles systems by formation of carbon–carbon and carbon–heteroatom bond. Some applications in organic chemistry include the synthesis of quinolines[2], spiro dihydroquinoline-oxindoles,[3] tetrahydrofurans,[4] trienes,[5] benzofurans[6] and dioxocanes.[7]

The complex $BF_3{\cdot}OEt_2$ is a clear and volatile liquid which boils at 126 °C,[8] may form explosive peroxides in contact with air or oxygen and reacts exothermically with water to form extremely flammable diethyl ether.

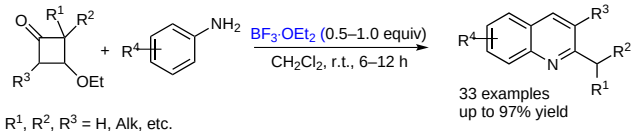
$BF_3{\cdot}OEt_2$ is commercially available, but it can be prepared by reaction between ethyl ether and the gaseous Lewis acid BF_3 (Scheme 1).



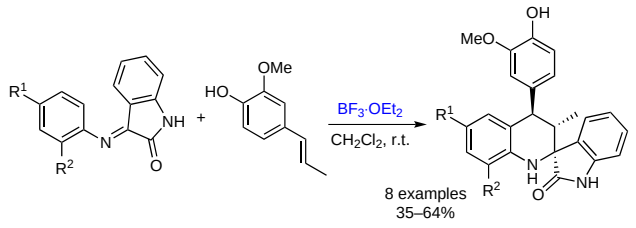
Scheme 1

Abstracts

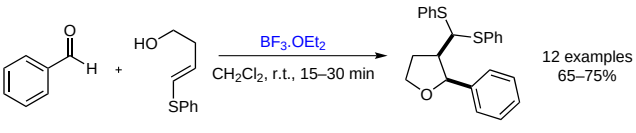
(A) Shan et al.[2] showed that it $BF_3{\cdot}OEt_2$ is useful for the preparation of a variety of substituted quinolines some of which are difficult to make via conventional approaches. An efficient one-step [3+3] annulation reaction at room temperature between 3-ethoxycyclobutanones and aromatic amines is realized. The reaction shows excellent reactivity, good functional group tolerance, complete regioselectivity, and high yields.



(B) Kouznetsov and co-workers[3] reported an efficient, easy, fast, and cheap way for the synthesis of the new spiro dihydroquinoline-oxindoles using the Povarov reaction. This method use $BF_3{\cdot}OEt_2$ for promoted imino-Diels–Alder cycloaddition between ketimine-isatin derivatives and *trans*-isoeugenol.



(C) Aldehydes undergo smooth cyclization with 4-(phenylthio)but-3-en-1-ol in the presence of $BF_3{\cdot}OEt_2$ to afford a novel class of 2,3-disubstituted tetrahydrofurans in good yields with all-*cis*-selectivity.[4] This method is simple, selective, and convenient, that provides a variety tetrahydrofurans in a single-step operation.



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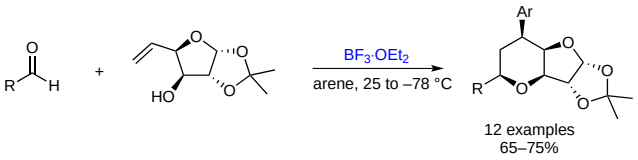
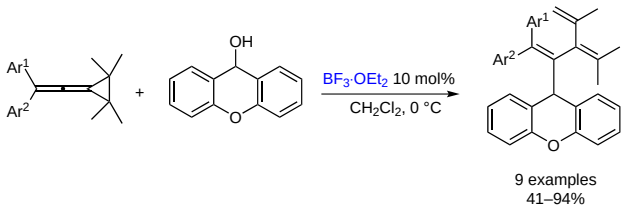
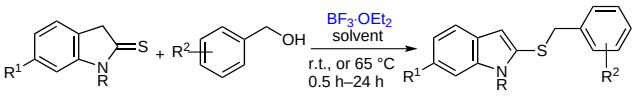
(D) Subba et al.[9] have developed a novel approach for the synthesis of 5,7-diarylhexahydro-2*H*-furo[3,2-*b*]pyrans via Prins Friedel–Crafts cyclization. In this reaction a D-glucose-based homoallylic alcohol reacts smoothly with various aldehydes in the presence of arenes and a catalytic amount of $BF_3{\cdot}OEt_2$ under mild conditions. This method provides an easy access for a new class of annulated pyran sugars in a single-step operation, which may find application in drug discovery and also in natural products synthesis.



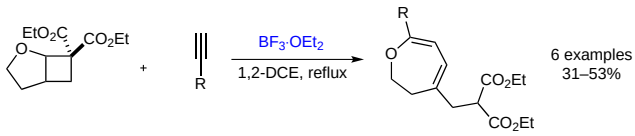
(E) $BF_3{\cdot}OEt_2$ promotes ring opening of vinylidenecyclopropanes which reacts with xanthydrol to give the corresponding conjugate triene derivatives in moderated to good yields.[5] Interesting transformation of these conjugate trienes has been disclosed in the presence of $BF_3{\cdot}OEt_2$ at 70 °C, affording a series of novel spiro-alkanes in moderate to good yields.



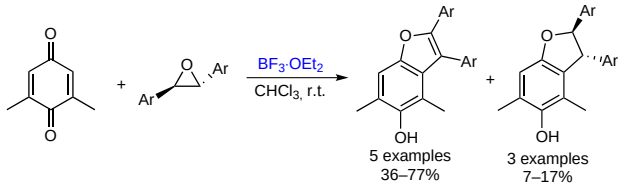
(F) Jha et al.[1] described the first example of a chemoselective S-benzylation of indoline-2-thiones under mild conditions, using a variety of benzyl alcohols and $BF_3{\cdot}OEt_2$. In this procedure the aryl substituent has effects on the reactivity of benzyl alcohols toward S-benzylation and the results of those effects were also discussed.



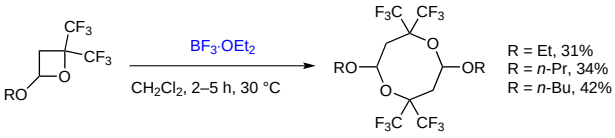
(G) Machin and Pagenkopf reported that in the presence of $BF_3{\cdot}OEt_2$ cyclobutane-1,1-diesters undergo a reaction with terminal alkynes to a quickly access to dihydro-oxepines.[10] These oxepines are formed through an intriguing rearrangement sequence. This methodology is currently being investigated for potential application towards the formation of fully saturated oxepines and the total synthesis of natural products.



(H) Kokubo et al. showed that $BF_3{\cdot}OEt_2$ promotes dehydrative cycloaddition reaction of benzoquinones with stilbene oxides to afford benzofurans and dihydrobenzofurans in good combined yields.[6]



(I) Petrov and Marshall developed the reaction of 2,2-bis(trifluoromethyl)-4-oxoetanes with $BF_3{\cdot}OEt_2$ in CH_2Cl_2 as solvent which results a spontaneous electrophilic [4+4] cyclodimerization with the formation of the corresponding dioxocanes isolated in 31–42% yield.[7]



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