

Boron trifluoride etherate in organic synthesis

Abstract

The Lewis acid boron trifluoride etherate has played an important role in organic synthesis. To accomplish the hydroxylation of double bond, cleavage of epoxides, esterification of acids and many cyclization reaction boron trifluoride etherate proved very useful compared to other Lewis acids. These organic reactions are frequently employed to achieve the synthesis of natural products. In addition, boron trifluoride etherate has also been utilized to realize ketalization, thioketalization, alkylation and many others organic reactions.

Keywords: boron trifluoride etherate, hydroboration-oxidation, epoxides, esterification, thioketalization, cyclization

Volume 3 Issue 1 - 2019

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Received: November 06, 2018 | Published: January 21, 2019

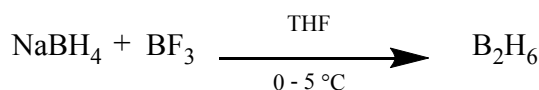
Introduction

The innumerable application of boron trifluoride etherate in organic synthesis^{1,2} encouraged us to write a micro review on this reagent. The commercially available boron trifluoride etherate (b.p. 126°C), a brown liquid, is very toxic by inhalation, causes severe burns, reacts violently with water, hot alkali or alkaline earth (not Mg) metals with incandescence. It can be purified by distillation. This review would discuss only four principal use of boron trifluoride etherate: (a) hydroboration-oxidation reaction, (b) cleavage and rearrangement of epoxides, (c) esterification (d) cyclization. In addition, some other minor uses of boron trifluoride etherate will be briefly described.

Applications of boron trifluoride etherate

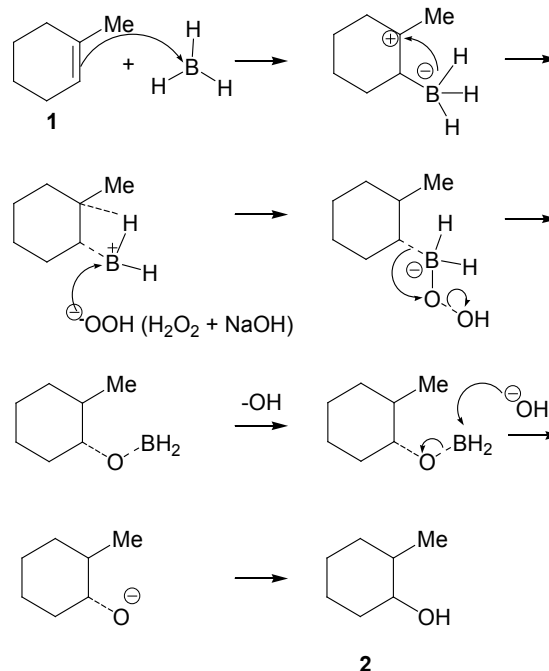
Hydroboration-oxidation reaction

The *cis* addition of diborane to an alkene bond provides an extremely useful method of hydration. Diborane can be generated by the addition of sodium borohydride to boron trifluoride etherate in tetrahydrofuran or ether at 0°-5°C. Diborane is the dimer of borane (BH₃) and is stable form of this reagent (Scheme 1).



Scheme 1 Obtention of Diborane from sodium borohydride

The addition of diborane to the alkene is extremely rapid and generally, the reagent adds from the less hindered of the two faces of the π system. The *cis* addition has been rationalized by a four center transition state. The borane complex resulting from the addition of diborane to an alkene is converted, with retention of stereochemistry, to an alcohol by treatment with basic hydrogen peroxide. Thus 1-methylcyclohexene 1 on hydroboration-oxidation leads the formation of trans-2-methylcyclo-hexanol 2. The mechanistic path has been depicted in (Scheme 2). The method for the conversion of alkene to alcohol by hydroboration-oxidation has been applied for the synthesis of many natural products. Few examples are illustrated below.

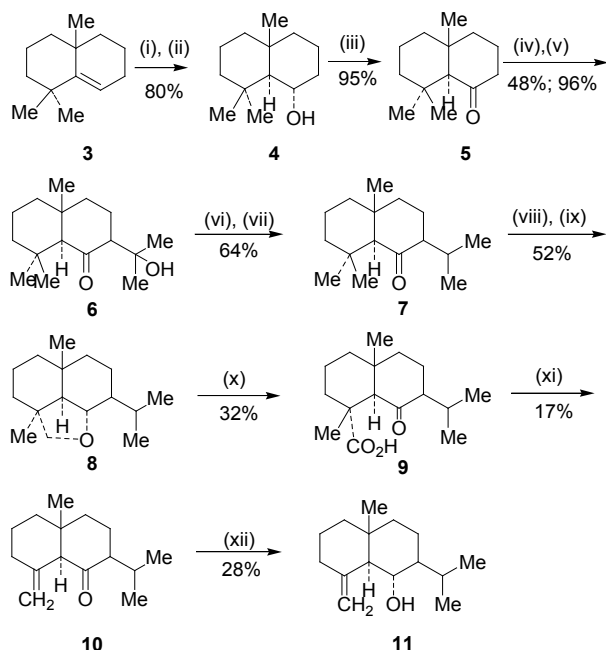


Scheme 2 Reaction mechanism for the formation of trans-2-methylcyclohexanol 2

Synthesis of (±) junenol and (±) acalomone

The use of hydroboration-oxidation reaction was observed by Banerjee and coworkers during the synthesis³ of eudesmone sesquiterpenes (±) junenol and (±) acalomone. In order to achieve the synthesis of these sesquiterpenes the alkene 3, was selected as starting material and subjected to hydroboration-oxidation to yield the alcohol 4 (Scheme 3). Ketone 5, obtained by the oxidation of the alcohol with Jones reagent⁴ was made to react with diethyl carbonate. The resulting product was treated with methyl lithium to obtain the ketol 6 whose conversion to the isopropyl ketone 7 was effected by dehydration

and hydrogenation respectively. Metal hydride reduction of the ketone followed by oxidation with lead tetraacetate⁵ in cyclohexane afforded the cyclic ether 8, which was converted to ketoacid 9 by oxidation with chromic acid and acetic acid. Decarboxylation with lead tetraacetate in benzene and pyridine followed by purification over 10% AgNO₃ impregnated silica gel afforded (±) acolamone 10. Reduction of acolamone 10 with sodium borohydride in methanol, followed by sublimation of the resulting product yielded junenol 11.



Scheme 3 Synthesis of eudesmone sesquiterpenes (±) junenol and (±)-acolamone

Reagents: (i) BF₃·Et₂O, NaBH₄, THF, 0–5°C; (ii) NaOH (10%), H₂O₂ (30%); (iii) CrO₃/HMPT; (iv) NaH, CO(OEt)₂, DME; (v) MeLi, Et₂O, reflux, 2h; (vi) HCl(conc), MeOH; (vii) H₂, PtO₂, MeOH; (viii) Na, EtOH, reflux; (ix) Pb(OAc)₄, C₆H₁₂; (x) CrO₃, AcOH; (xi) Pb(OAc)₄, C₆H₆, Py, reflux; (xii) NaBH₄, EtOH.

Synthesis of pisiferic acid

The use of hydroboration-oxidation has been recorded during the synthesis of pisiferic acid,⁶ a tricyclic diterpene which shows antibacterial activities against all gram-positive bacteria tested.⁷ The synthetic route has been depicted in Scheme 4. Hydroboration-oxidation of the alkene 13, prepared from the known⁸ ketoalcohol 12, was oxidized with Jones reagent⁴ and reduced respectively with metal hydride to give alcohol 14. Oxidation with lead tetraacetate in benzene with 250W tungsten lamp gave the cyclic ether 15. The cleavage of the cyclic ether with zinc, zinc iodide and acetic acid⁸ furnished pisiferol 16. The transformation of the pisiferol to the ester 17 was achieved in six steps:

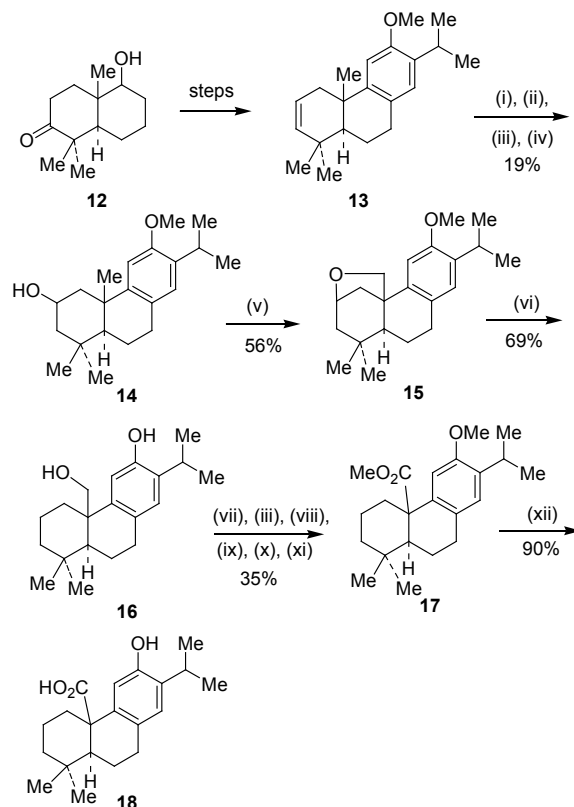
- (i) Methylation with dimethyl sulfate
- (ii) Oxidation with Jones reagent
- (iii) Esterification with diazomethane
- (iv) Reduction with sodium borohydride
- (v) Tosylation
- (vi) Detosylation

The ester 17 was converted into pisiferic acid 18 by heating with aluminium bromide and ethane thiol.

The hydroboration-oxidation reaction has been applied for the synthesis of (±) eudes-4(14),7(11)-diene-8-one,⁹ taxodione,¹⁰ norditerpene alcohols¹¹ and many other terpenes.¹² These examples clearly indicate the use of boron trifluoride etherate in the conversion of the alkenes into alcohols and subsequently their transformations into the terpenoid compounds.

Cleavage of epoxides

The epoxides can be cleaved by several reagents. The Lewis acid borontrifluoride etherate has also been used for the cleavage of epoxides and in many cases the resulting product rearranges to ketone. The cleavage of epoxides is also accompanied by cyclization. In this review the cleavage of some epoxides with boron trifluoride etherate and the use of the resulting products in the synthesis of natural products have been discussed.



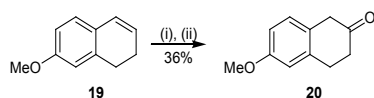
Scheme 4 Synthesis of pisiferic acid 18

Reagents: (i) BF₃·Et₂O, NaBH₄; (ii) NaOH (10%), H₂O₂ (30%), H₂SO₄-HCrO₄; (iii) LiAlH₄, THF; (iv) Pb(OAc)₄, CaCO₃, C₆H₆, 250W tungsten lamp; (v) Zn, ZnI₂, MeCOOH; (vi) MeSO₄, Me₂CO; (vii) H₂SO₄-HCrO₄; (viii) CH₂N₂, Et₂O; (ix) NaBH₄, MeOH; (x) TsCl, Py; (xi) NaI, Zn dust, DMF; (xii) AlBr₃, (CH₃SH)₂.

Synthesis of 6-methoxy-2-tetralone

The cleavage of epoxide with boron trifluoride etherate has been utilized¹³ for the synthesis of 6-methoxy-2-tetralone 20 (Scheme 5), an important selected starting material for the synthesis of many organic compounds. Epoxidation of the alkene¹³ 19 followed by treatment of the crude product in dichloromethane with boron trifluoride etherate afforded the tetralone 20 in 36% yield. When the cleavage was tried

with sulfuric acid the yield of the teralene 20 was improved (39%) along with the formation of other secondary products and thus the chromatographic purification was very laborious.

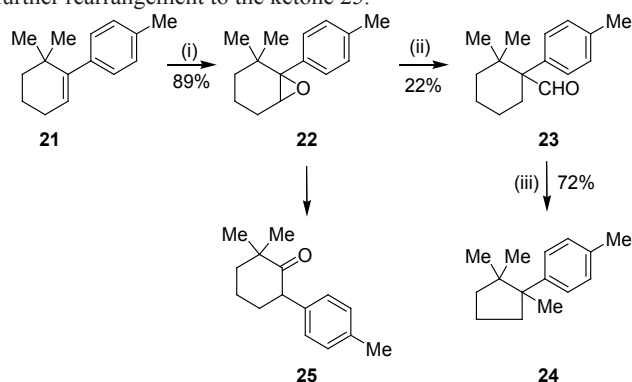


Scheme 5 Synthesis of 6-methoxy-2-teralene 20

Reagents: (i) MCPBA, CH_2Cl_2 ; (ii) $\text{BF}_3\cdot\text{OEt}_2$

Synthesis of cuprane

The rearrangement of epoxides by boron trifluoride etherate proved very useful during the synthesis¹⁴ of sesquiterpene cuprane. The synthetic route is described in Scheme 6. 6,6-dimethyl-1-p-tolylcyclohexene 21 on epoxidation afforded the epoxide 22 in good yield which on treatment with boron trifluoride etherate in benzene yielded the aldehyde 23 in low yield. The semicarbazone of the aldehyde was heated with potassium hydroxide to furnish the sesquiterpene cuprane 24 in acceptable yield. The synthesis is attractive due to its brevity in steps. The conditions used for the rearrangement of the epoxide 22 are critical because it has the tendency to undergo further rearrangement to the ketone 25.



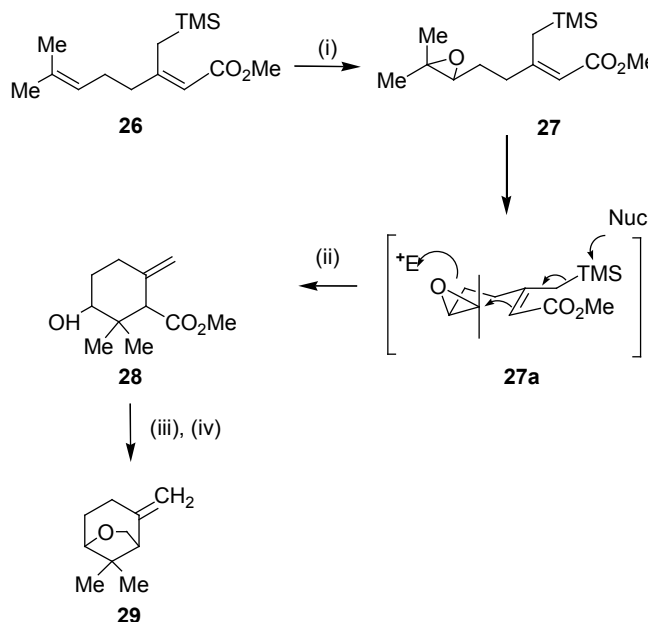
Scheme 6 Synthesis of cuprane

Reagents: (i) PhCO_3H , CHCl_3 ; (ii) C_6H_6 , $\text{BF}_3\cdot\text{OEt}_2$; (iii) $\text{NH}_2\text{NHCONH}_2$, KOH

Synthesis of (±) karahana ether

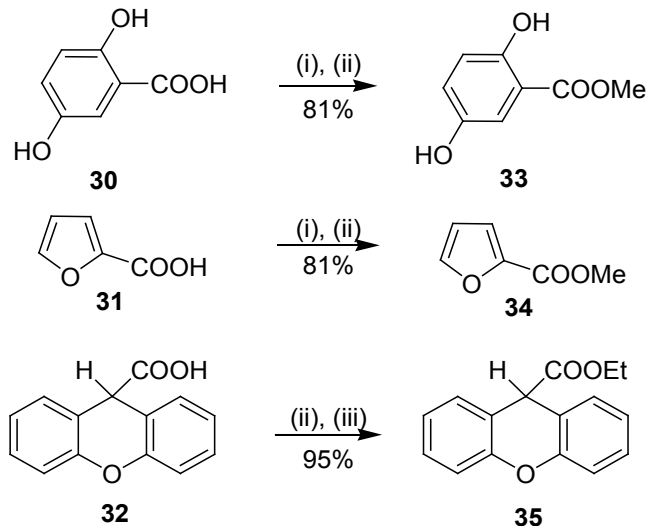
Boron trifluoride etherate was also used for the cleavage of epoxide during the synthesis¹⁵ of karahana ether, a volatile monoterpene which was isolated¹⁶ from Japanese hops. The synthetic route is described in Scheme 7. The epoxide 27, obtained from the diene 26, on being treated with boron trifluoride etherate underwent cyclization yielding the product 28. The cyclization probably occurred through the intermediate 27 (i). Metal hydride reduction afforded diol which on tosylation yielded karahanaether 29. The yield is unspecified. The cleavage of epoxides have been utilized for the synthesis of many terpenes like rosenolactone,¹⁷ cyperolone,¹⁸ maritimon.¹⁹

esterification of carboxylic acids. Dymicky²² prepared several formats in high yield from formic acid and alcohol in the presence of a catalytic amount of boron trifluoride-methanol complex. The other catalysts e.g. sulfuric acid, *p*-toluene sulfonic acid was not so efficient like boron trifluoride-methanol complex.



Scheme 7 Synthesis of (±) Karahana ether

Reagents: (i) MCPBA; (ii) $\text{BF}_3\cdot\text{OEt}_2$; (iii) LiAlH_4 ; (iv) TsCl , Py



Scheme 8 Esterification of acids 32-35

Reagents: (i) MeOH; (ii) $\text{BF}_3\cdot\text{OEt}_2$; (iii) EtOH

Esterification is a frequently used reaction for the synthesis of many organic compounds. Boron trifluoride etherate-alcohol is a very convenient reagent for the esterification of many *p*-amino benzoic acids, aromatic, heterocyclic and unsaturated acids.²⁰ In some esterification reactions the use of this reagent provided superior yield compared with other reagents. Some examples are given in Scheme 8. The acids 30-32 were converted to the esters 33-35 respectively in high yield on treatment with boron trifluoride etherate-alcohol reagent. Marshall and collaborators²¹ used the same reagent for the

Jackson and collaborators²³ have developed an efficient method for the conversion of alcohols 37-39 and acids 40-42 directly to the corresponding *t*-butyl derivatives in good yield using *t*-butyl trichloroacetimidate 36 in the presence of a catalytic amount of boron trifluoride etherate as exhibited in Scheme 9. This method functions better with the acid sensitive groups than the traditional methods using isobutene. Less hindered hydroxyl group of a diol can be protected and also is amenable to small scale work (avoiding the handling of gaseous isobutene). The *t*-butyl 2,2,2-trichloroacetimidate 36 is

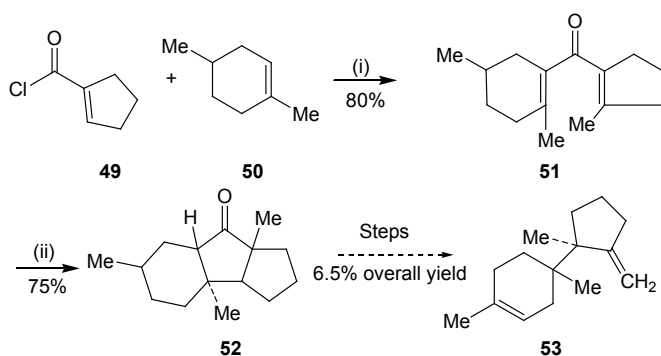
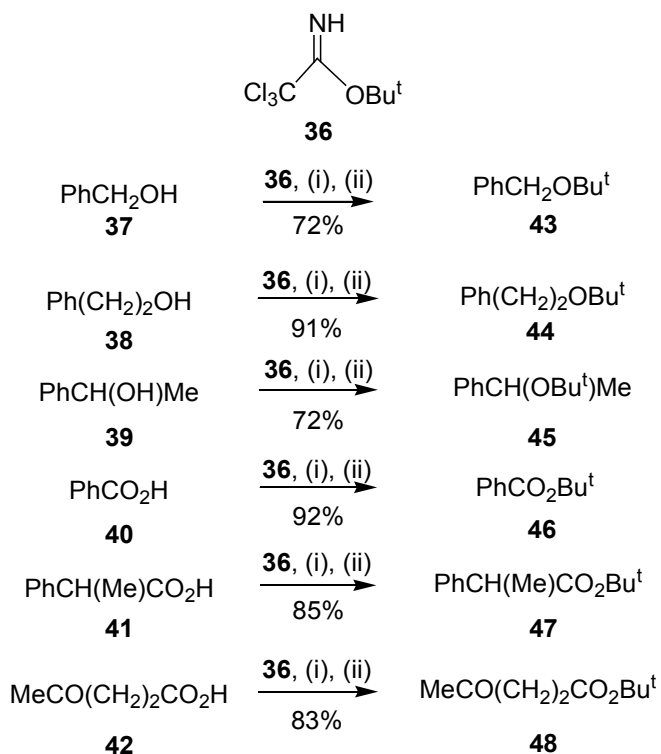
readily prepared by the addition of *t*-butanol to trichloroacetonitrile. Most of the experiments were carried out in presence of a mixture of dichloromethane and cyclohexane. Acetic anhydride in presence of boron trifluoride etherate has been utilized for the acetylation of hydroxyl group.²⁴

Cyclization

The boron trifluoride etherate has played an important role in cyclization of many, carboxylic acids, allenes etc. The following few examples will illustrate the role of boron trifluoride etherate as cyclizing agent. The acid chloride 49 and alkene 50 were condensed to yield divinyl ketone²⁵ 51 which underwent Nazarov cyclization^{26,27} furnishing cyclic ketone 52 which was converted to the sesquiterpene trichodiene 53 (Scheme 10).

Scheme 9 Conversion of alcohols and acids from *t*-butyl derivatives.

Reagents: 36, (i) $\text{BF}_3 \cdot \text{Et}_2\text{O}$, (ii) CH_2Cl_2 , C_6H_{12}

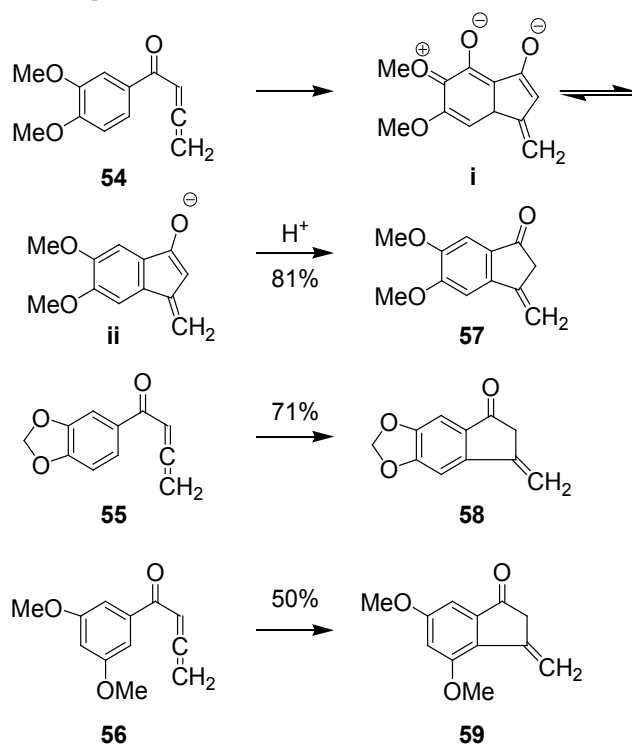


Scheme 10 Synthesis of sesquiterpene trichodiene 53

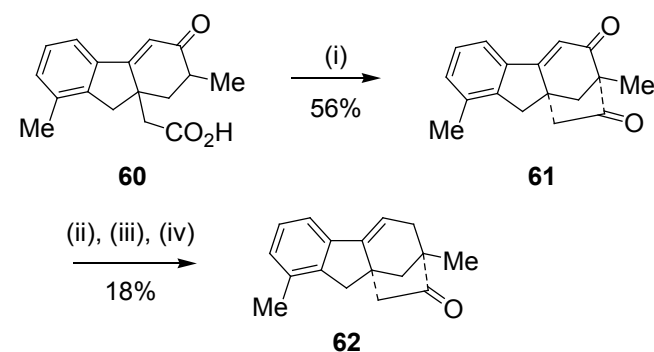
Reagents: (i) SnCl_4 , NaOMe ; (ii) $\text{BF}_3 \cdot \text{Et}_2\text{O}$

Several allenyl aryl ketones undergo cyclization with boron trifluoride etherate affording methylene benzocyclopentenone *via* a new 5-endo-mode cyclization.²⁸ The ketones 54-56 afforded benzocyclopentenones 57-59 respectively (Scheme 11). Probably the transformation occurred as shown in the cyclization of allenyl aryl ketone 54 into 57. It can be observed that the presence of substituent groups in aromatic ring determines the yield of the cyclized product. Kos and Loewenthal²⁸ reported the cyclization of the acid 60 with boron trifluoride etherate to the ketone 61 which was converted gibberone 62 (Scheme 12) in three steps:

- (i) Ketalization
- (ii) Huang-Minlon reduction and
- (iii) Acid hydrolysis. The above mentioned examples exhibit the use of boron trifluoride etherate in the cyclization of organic compounds



Scheme 11 Synthesis of Cyclopentenones



Scheme 12 Synthesis to gibberone

Reagents: (i) $\text{BF}_3 \cdot \text{Et}_2\text{O}$; (ii) (a) $\text{C}_2\text{H}_6\text{O}_2$; (b) DEG, N_2H_4 , KOH, 190-200°C; (c) H^+

Miscellaneous uses

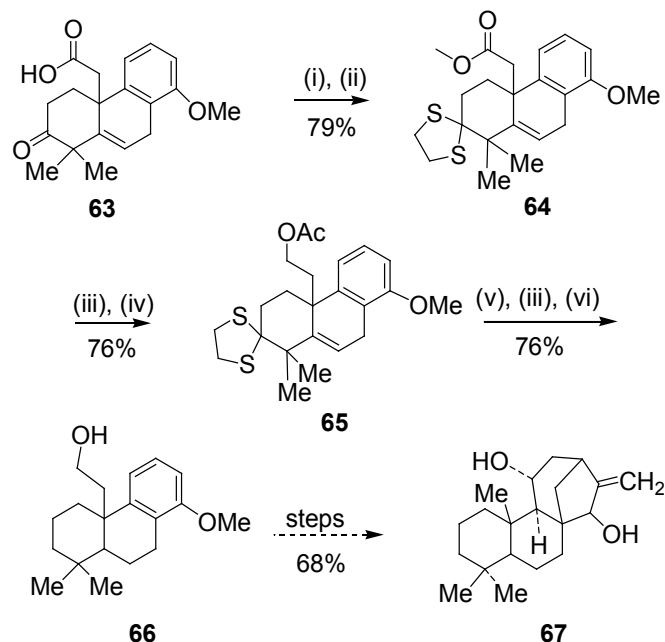
In addition of the above mentioned reactions the following reactions also have been performed but not frequently employing boron trifluoride etherate.

(A) Thioketalization and ketalization

Thioketalization and ketalization reaction are very important reactions for organic synthesis. Some examples are given below. The acid 63 (Scheme 13) on esterification and thioketalization respectively afforded the compound 64 which on metal hydride reduction and acetylation respectively yielded the acetate 65. The conversion of the acetate into the alcohol 66 was accomplished in three steps:

- Desulphurization
- Metal hydride reduction
- Catalytic hydrogenation

The alcohol 66 was utilized for synthesis 29 of kaurenediol 67.



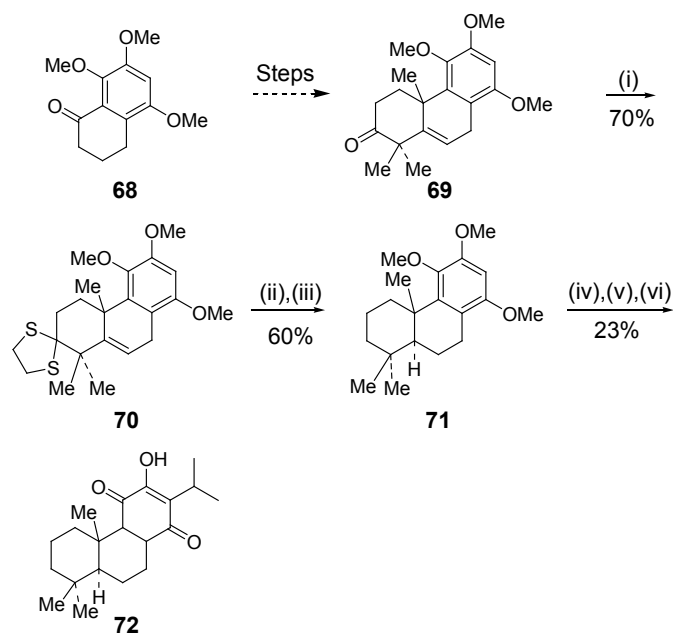
Scheme 13 Synthesis of Kaurenediol 67

Reagents: (i) CH_2N_2 , Et_2O ; (ii) $(\text{CH}_2\text{SH})_2$, BF_3OEt_2 ; (iii) LiAlH_4 , Et_2O (iv) AC_2O , Py ; (v) Ra-Ni ; (vi) H_2 , 10% Pd/C .

Thioketalization reaction was also applied^{30,31} for the synthesis of non-aromatic abietane type quinone royleanone which shows the cytotoxic activity against Eagle's KB strain of human carcinoma of the naso-pharynx. The synthetic route is described in (Scheme 14). The ketone 69, prepared, from the ketone 68, was subjected to thioketalization to obtain the compound 70. Desulphurization followed by catalytic hydrogenation yielded 71 whose conversion to royleanone 72 was accomplished in three steps:

- Demethylation with boron tribromide
- Heating the resulting compound in refluxing benzene with bubbling oxygen gas and
- Isopropylation with isobutyl peroxide in acetic acid. It is worthwhile to mention thioketalization reaction catalyzed by boron trifluoride etherate has also been applied for the synthesis

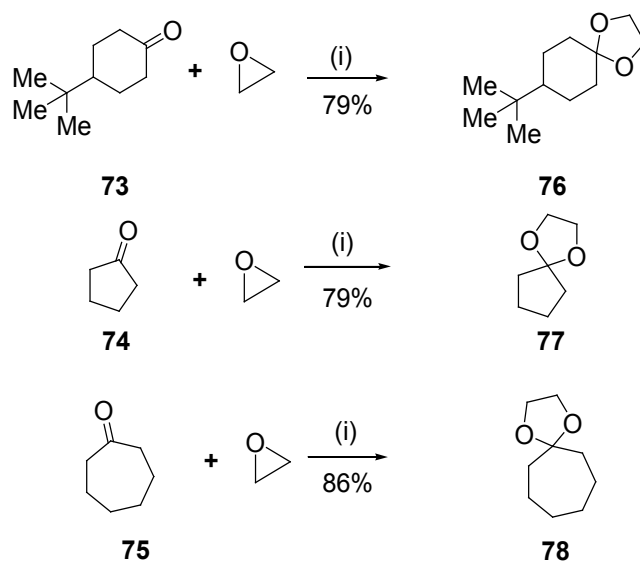
of dehydroabietic acid by Stork and Schulberg,³² phyllocladene by Church and Ireland,³³ Mori and Matsui,³⁴ and many others.¹²



Scheme 14 Synthesis of non-aromatic abietane type quinone

Reagents: (i) $(\text{CH}_2\text{SH})_2$, BF_3OEt_2 ; (ii) Ra-Ni , boiling ethanol; (iii) 10% (Pd-C) , MeCOOH ; (iv) BBr_3 , CH_2Cl_2 ; (v) C_6H_6 , O_2 ; (vi) $(\text{MeCHCO}_2)_2$

Like thioketalization, boron trifluoride etherate has been used as catalyst for the reaction of ketones with oxirane to yield ketals.³⁵ Thus the ketones (73-75) were converted to the ketals (76-78) respectively in high yield (Scheme 15). The use of epoxides for ketal formation offers the advantage of being extremely gentle, operating at room temperature and under protic conditions. Diethylene ortho carbonate converts ketones and aldehydes into their corresponding acetals in good yields at room temperature using slightly wet boron trifluoride etherate.³⁶ It is particularly suitable for *ortho-hydroxy* aromatic aldehyde.

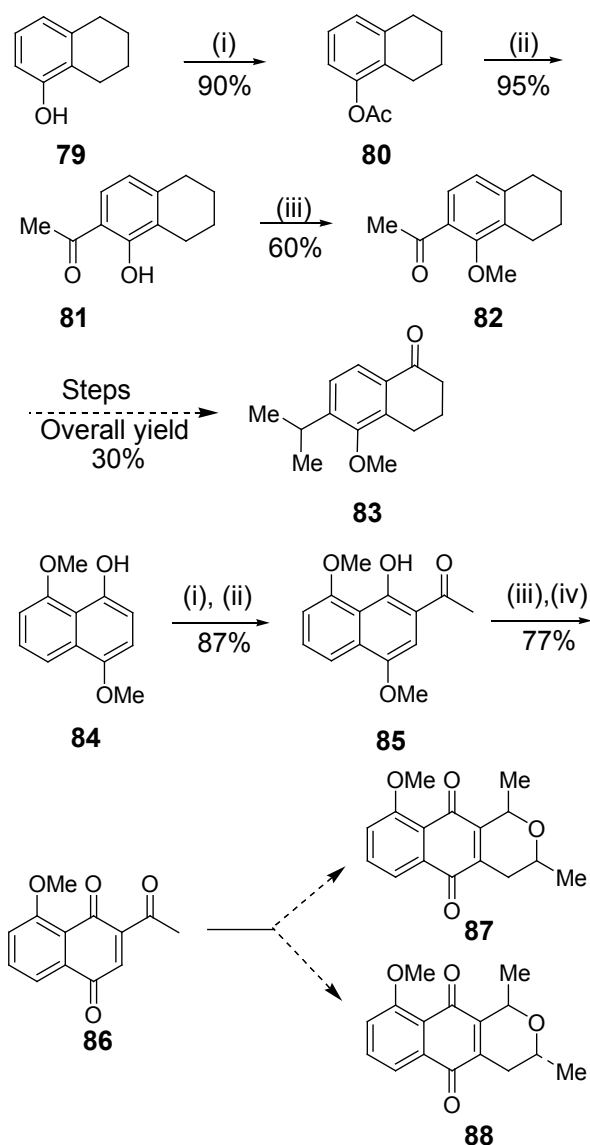


Scheme 15 Synthesis of ketals from ketones

(i) BF_3OEt_2 , CH_2Cl_2 , 25°C .

(B) Molecular rearrangements

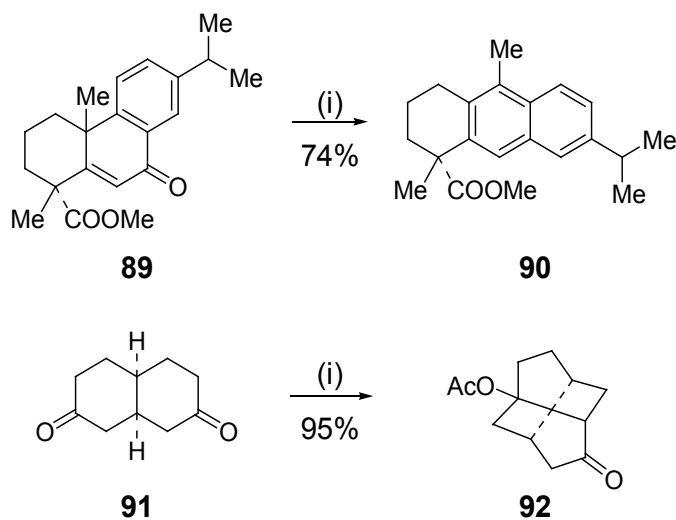
Many organic compounds undergone transformation in presence of boron trifluoride etherate. The following examples illustrate the rearrangements originated by boron trifluoride etherate. The acetate **80** prepared from hydroxyl tetralin **79** underwent Fries rearrangement³⁷ on heating at 125°C with boron trifluoride etherate in a microwave oven. The resulting tetrahydronaphthol³⁸ **81** (Scheme 16) was methylated to yield the compound **82** and finally converted to the already reported³⁹ tetralone **83** (Scheme 16). Thus an alternative route³⁸ was developed for the tetralone **83** which proved very useful for the synthesis³⁹ of bioactive diterpene (+) triptoquinone A and its analog (+) triptin. Similarly, the Fries rearrangement with boron trifluoride etherate was applied⁴⁰ to the acetate, prepared from the naphthol **84**. The compound **85** was treated with cerium ammonium nitrate (CAN) to obtain the quinone **86**. The quinone was utilized for the synthesis of eleutherins⁴⁰ **87** and isoeleutherin **88** (Scheme 16).



Scheme 16 Synthesis of quinones from Naphthol

Reagents: (i) Ac_2O , Py; (ii) $\text{BF}_3 \cdot \text{Et}_2\text{O}$; (iii) Me_2SO_4 , Me_2CO ; (iv) CAN, MeCN

Matsumoto and collaborators⁴¹ reported a novel rearrangement of hydrophenanthrene into hydroanthracene with boron trifluoride etherate. Thus the alcohol obtained by the metal hydride reduction of the enone **89** on treatment with boron trifluoride etherate suffered an interesting rearrangement yielding anthracene **90**. This method for the synthesis of anthracene was applied to the synthesis of biologically active linear abietane diterpenes. Deslongchamps⁴² reported a very interesting rearrangement of diketone **91** to 8-acetoxy-4-twistanone **92** on treatment with a mixture of acetic acid, acetic anhydride and boron trifluoride at room temperature. The compound **92** is the first twistane derivative having a functional group at a bridge position (Scheme 17).



Scheme 17 Rearrangement of diketones

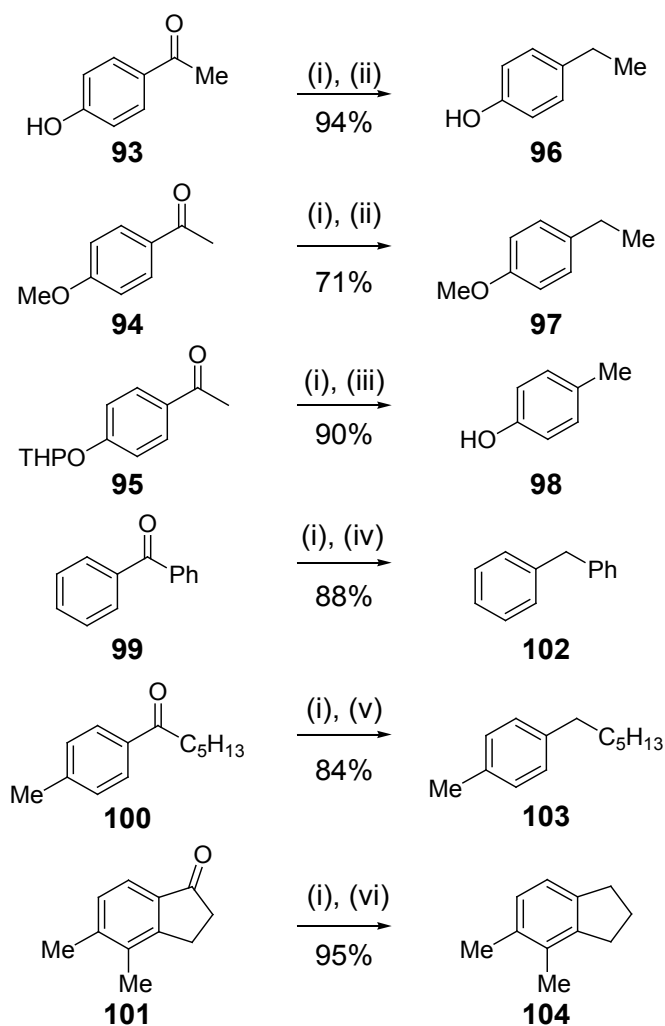
Reagents: (i) AcOH , Ac_2O , $\text{BF}_3 \cdot \text{OEt}_2$

Srikrishna and collaborators⁴³ reported one-step method for the conversion aryl ketones into the corresponding hydrocarbons by stirring with sodium cyanoborohydride in presence of two to three equivalents of boron trifluoride etherate. Thus the ketones (93-95) were converted into the corresponding hydrocarbons (96-98) respectively in high yield. These reactions were conducted at room temperature. High temperature was also used for the deoxygenation of some aryl ketones e.g. (99-101) into the hydrocarbons (102-104) respectively (Scheme 18).

A mixture of boron trifluoride etherate and acetic anhydride at 0° or below has been found to cleave different types of steroidal methyl ethers.⁴⁴ Allylic and homoallylic ethers give the corresponding acetates in high yield. The completely saturated ethers give the acetate with retention of configuration as the main substituent product, but the epimeric acetate and elimination products are also obtained. A very interesting result was obtained when the demethylation experiment was tried with 4,8-dimethoxy-1-tetralone⁴⁵ **105** with boron trifluoride etherate and acetic anhydride. The tetralone underwent aromatization yielding the acetate **106** not the expected acetate **107** (Scheme 19). On similar treatment the tetralone **108** afforded the acetate **109**. These observations did not agree with the reported observation of Narayanan and Iyer on steroidal ethers.⁴⁴

One of the most interesting applications of boron trifluoride etherate consists in the unprecedented alkylation of carboxylic acids

in the absence of alcohols.⁴⁶ Many aromatic and aliphatic carboxylic acids were readily alkylated in short time. It was also observed that *ortho*-substituted hydroxyl groups of carboxylic were not affected by alkylation but those of *Meta*- and *para*-substituted carboxylic acids were partially etherified. In addition alkylation reaction was carried out in presence of several functional groups such as halogens, amino and nitro groups. Some examples are given below (Scheme 20). Thus the acids (110-112) were alkylated to obtain the alkylated products (113-115) respectively.

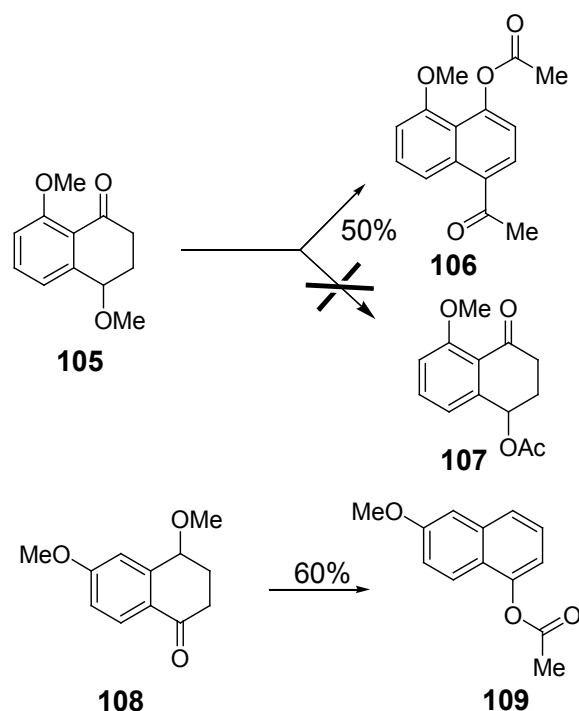


Scheme 18 Conversion of the aryl ketones into the corresponding hydrocarbons

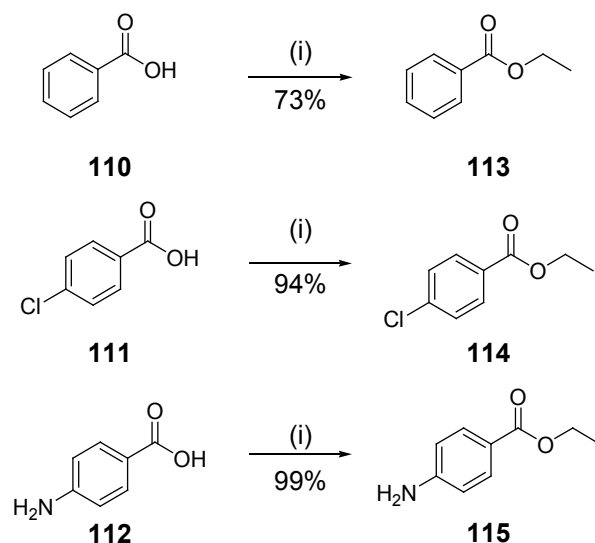
Reagents: (i) NaCNBH_3 , $\text{BF}_3 \cdot \text{OEt}_2$; (ii) RT, 12 h; (iii) RT, 8 h; (iv) 65°C , 8 h; (v) 65°C , h; (vi) 65°C , 4 h.

Conclusion

This mini review focuses some of the applications of the boron trifluoride etherate in organic synthesis. The use of boron trifluoride etherate would continue owing to its operational simplicity and low cost. We believe the many of the above mentioned reactions could not have been accomplished without boron trifluoride etherate. Some of the products mentioned above have received use in natural product synthesis. It is necessary to indicate that many important applications of boron trifluoride etherate have been omitted in this review due to the limitation of space. We are sure that the information's discussed



Scheme 19 Aromatization of tetralones
Reagents: BF_3 , Et_2O , Ac_2O



Scheme 20 Alkylation reaction
Reagents: (i) $\text{BF}_3 \cdot \text{OEt}_2$, Reflux

would serve the need of organic chemists engaged in searching new applications of boron trifluoride etherate in organic synthesis.

Acknowledgments

The authors gratefully acknowledge the receipt of the reprint on alkylation from Dr. Wayiza Masamba, Department of Chemical and Physical Sciences, Walter Sisulu University, Nelson Mandela Drive, South Africa and collaboration of Mr. José Gregorio, Biblioteca IVIC, Caracas Venezuela for literature references.

Po S. Poon also thanks CONICYT PIA/APOYO CCTE AFB170007 and CONICYT FONDECYT 1161068.

Conflicts of interest

Authors declare that there is no conflict of interest.

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