Reagents for the synthesis of alkenes from carbonyl compounds: applications in the synthesis of terpenoid compounds

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Abstract

The carbon-carbon double bond has been introduced by replacing carbonyl group employing various reagents in several decalones and tetralones. The resulting unsaturated compounds have been utilized for the synthesis of natural products related to diterpenes triptolide, taxodione and sesquiterpenes, herbertene, cuauhtemone, warburganal, drim-8-en-7-one, occidol, mansonone F and biflorine.

Keywords: Halide, tosylate, mesylate, alkene, dimethylformamide, 2,4-pentanediol

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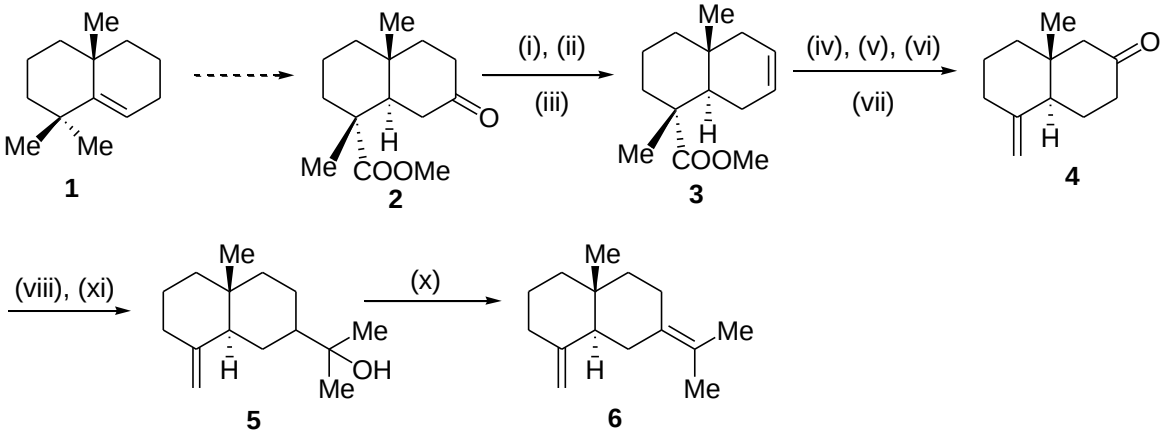
1. Introduction

The formation of carbon-carbon double bond is of fundamental importance in organic synthesis because it allows the introduction of a wide variety of functional groups. As a result, many reactions and reagents have been developed for carbon-carbon double bond formation. Several reagents were utilized by us to obtain alkenes from the carbonyl compounds. The present account is largely a survey of the reagents utilized between 1990-2012 at the Department of Chemistry, IVIC, Caracas and University of Zulia, Maracaibo, Venezuela, for the synthesis of alkenes from carbonyl compounds and their utility in the synthesis of terpenoid compounds.

2. Reagents for the Conversion of Carbonyl into Alkene

2.1. Lithium bromide (LiBr), lithium carbonate (Li_2CO_3) and dimethylformamide (DMF)

The combination of LiBr and Li_2CO_3 in DMF is a powerful reagent for detosylation to yield alkene. Therefore for the conversion of the ketone into an alkene, a carbonyl group is converted into a tosyl group by reduction and detosylation. The combination of these reagents has been frequently used in our laboratory. Some examples are cited below: Ketoester[1] **2**, prepared from the octalin **1**, on reduction with sodium borohydride in methanol yielded a mixture of alcohols whose tosyl derivative on heating with LiBr, Li_2CO_3 and DMF afforded the alkene[1] **3** which was converted into the methylene decalone[2] **4** in four steps (bromohydrin reaction, oxidation, dehydrohalogenation, and oxidative decarboxylation).

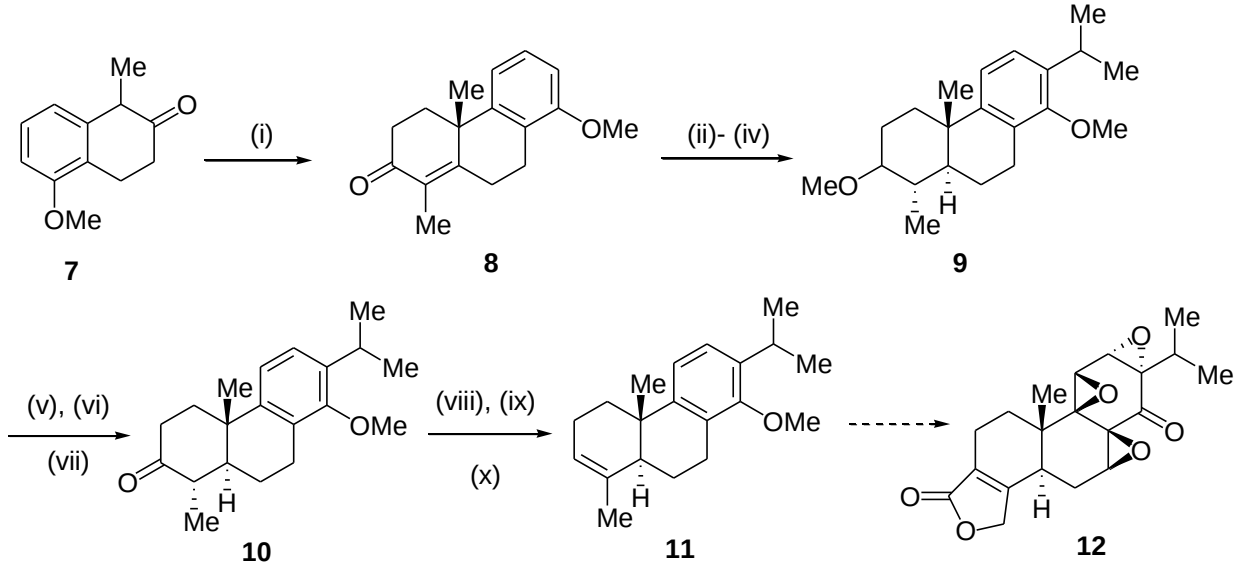


Reagents: (i) $NaBH_4$, MeOH; (ii) TsCl/Py; (iii) Li_2CO_3, LiBr, DMF; (iv) NBS, DMSO; (v) CrO_3, Me_2CO_3, (vi) collidine, (vii) $Pb(OAc)_4$, C_6H_6, Py; (viii) $CO(COOMe)_2$, DME, NaH; (ix) MeLi, Et_2O (2M); (x) $SOCl_2$, Py

Scheme 1

Methoxycarbonylation of the decalone **4** followed by treatment of the resulting compound with Grignard reagent produced alcohol **5** which on dehydration yielded[3] (±)-eudes-4(14),7(11)-diene-8 **6** whose alternative synthesis was already reported.[4] The synthetic route developed[1,3] by us is described in Scheme 1. The natural product **6**, which was isolated[5] from *Atraclyodes rhizones*, exhibits significant anti-inflammatory activity.

The combination of LiBr, Li_2CO_3 in DMF was also used for the synthesis of alkene **11**, a potential intermediate for the synthesis of triptolide **12** which has abietane skeleton and exhibits cytotoxic activity. The unsaturated ketone[6] **8**, obtained by the condensation of the tetralone **7** with 1-chloro-3-pentanone, was converted into the compound **9** in three steps (reduction[7], methylation, isopropylation[8]) which on being subjected to demethoxylation,[9] oxidation and methylation respectively yielded the ketone **10.** The conversion of the ketone to the alkene[10] **11** in 55% yield was accomplished by reduction, tosylation and detosylation respectively. The alkene **11** has already been converted[11] to triptolide **12** which is a promising anticancer compound. The synthetic route is described in Scheme 2.

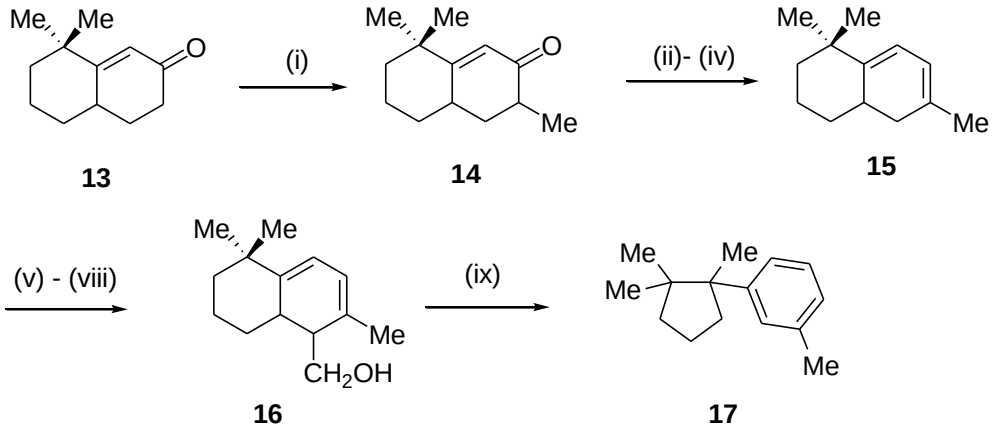


Reagents: (i) 1-chloro-3-pentanone; (ii) Na, *n*-propanal; (iii) MeI, NaH, THF; (iv) isopropanal, PPA; (v) MeSiCl, NaI, MeCN; (vi) CrO_3, H_2SO_4; (vii) Me_2SO_4, K_2CO_3, Me_2CO; (viii) $NaBH_4$, MeOH; (ix) TsCl/ Py; (x) Li_2CO_3, DMF

Scheme 2

The use of LiBr, Li_2CO_3 and DMF in detosylation for the synthesis of alkene has also been observed during our realization of the synthesis[1] of sesquiterpene (±)-herbertene **17**, which possesses a 1,1,2-trimethyl-2-*m*-tolycyclopentane structure. The known[12] ketone **13** on methylation afforded the methylated ketone **14 (**Scheme 3**)** whose transformation to the diene **15** was accomplished by reduction, tosylation and detosylation respectively. The α,β-unsaturated ketone obtained by oxidation of the diene **15** on cyanation and reduction respectively yielded an aldehyde

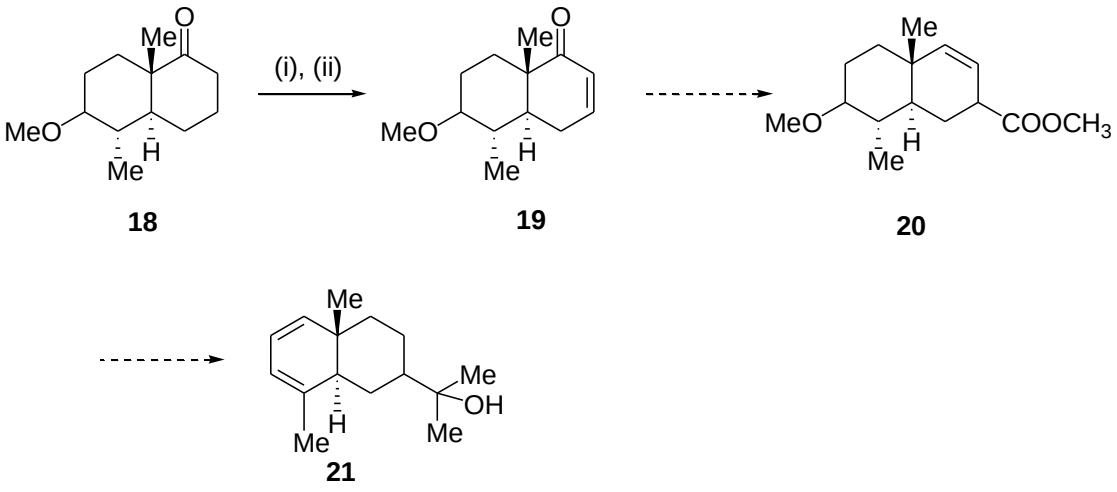
which was further reduced[13] to obtain the alcohol **16**. Frater[14] observed that the alcohol **16** on treatment with perchloric acid underwent transformation yielding the aromatic sesquiterpene herbertene **17**. Thus an alternative route[15] of the alcohol **16** prepared from the diene **15** constitutes a potential intermediate for the natural product (±)-herbertene **17**.



Reagents: (i) LDA, HMPA,MeI, -70 ^{o}C; (ii) $NaBH_4$, MeOH;(iii) TsCl/ Py; (iv) LiBr, Li_2CO_3, DMF; (v)CrO_3, Py; (vi) C_4H_9OK, t-BuOH, Tosmic, DMF; (vii) DIBAL, Toluene; (viii) $NaBH_4$ - Alox complex; (ix) $HClO_4$

Scheme 3

The combination of LiBr, Li_2CO_3 and DMF has also been utilized for dehydro-bromination to introduce double bond in organic molecule. Thus the reported[16] ketone **18** on bromination yielded bromoketone which on dehydrobromination with LiBr, Li_2CO_3 and DMF afforded unsaturated ketone[17] **19** whose conversion to the olefin ester **20** was accomplished without any difficulty using standard organic reactions. The unsaturated ester may serve as a potential intermediate for the synthesis of the racemic occidentalol **21** (Scheme 4), a eudesmane-type sesquiterpene, isolated from the wood of Eastern white cedar (*Thuja occidentalis L.)* and characterized by the presence of *cis*-fused decalin system and a homo annular 1,3-diene unit in the molecule.[18]

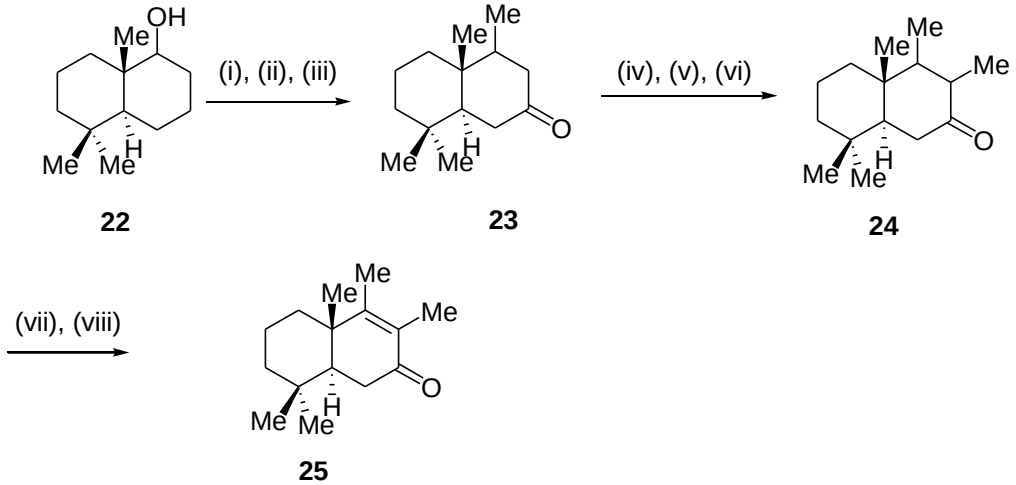


18 **19** **20** **21**

Reagents: (i) $C_5H_6NBr_3$, EtOH, $CHCl_3$; (ii) LiBr, Li_2CO_3, DMF

Scheme 4

During the synthesis[19] of the drimane sesquiterpene drim-8-en-7-one (Scheme 5) the utility of the reagent LiBr, Li_2CO_3 and DMF in dehydrohalogenation has also been noted. The already reported[20] alcohol **22** was converted to the ketone **23** in three steps (dehydration, oxidation and conjugate methylation). Its conversion to the ketone **24** was realized by ethoxycarbonylation, methylation and decarboxylation respectively. Bromination of **24** followed by dehydrobromination with LiBr, Li_2CO_3 and DMF proved useful in the introduction of double bond at the C-8 and C-9 of the compound **24** yielding drim-8-en-7-one **25** in good yield which is a sesquiterpene and previously synthesized from drimenol.[21]



22 **23** **24** **25**

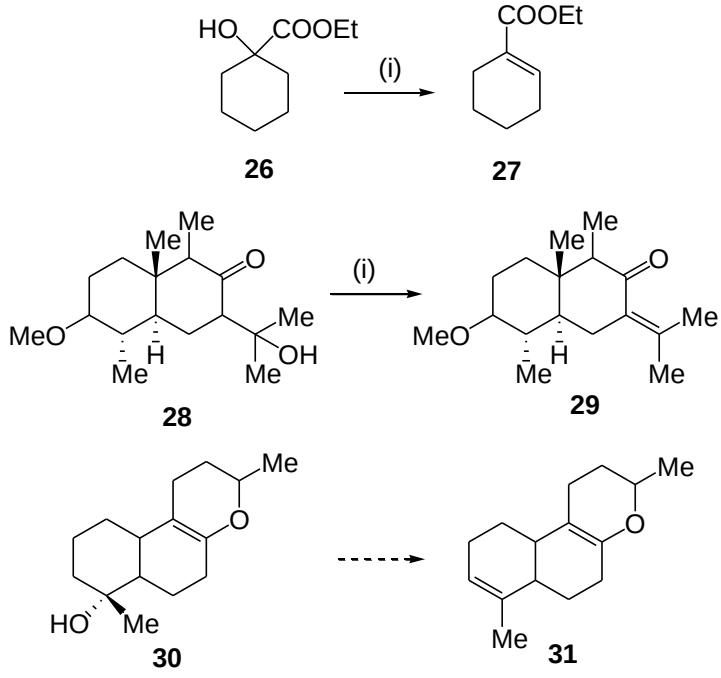
Reagents: (i) PTSA on silica gel, $CHCl_3$; (ii) CrO_3, 3,5-DMP; (iii) $MeLiCu_2$; (iv) $CO(COOEt)_2$, NaH, DME; (v) DMF, NaH, MeI, MeCOOH; (vi) DMSO, LiCl, H_2O, 170 - 180 ^oC; (vii) Br_2, $CHCl_3$, MeCOOH; (viii) LiBr, Li_2CO_3, DMF

Scheme 5

Thus it can be seen that the combination of the LiBr, Li_2CO_3 and DMF is an important reagent for detosylation and dehydrobromination thus for the introduction of double bond in a suitable position of organic molecule yielding the alkenes **3**, **11**, **15**, **19** and **25** which have been utilized for the synthesis of potential intermediate for natural products related to sesquiterpenes and diterpenes.

2.2. Thionyl chloride ($SOCl_2$), phosphorus oxychloride ($POCl_3$) and pyridine

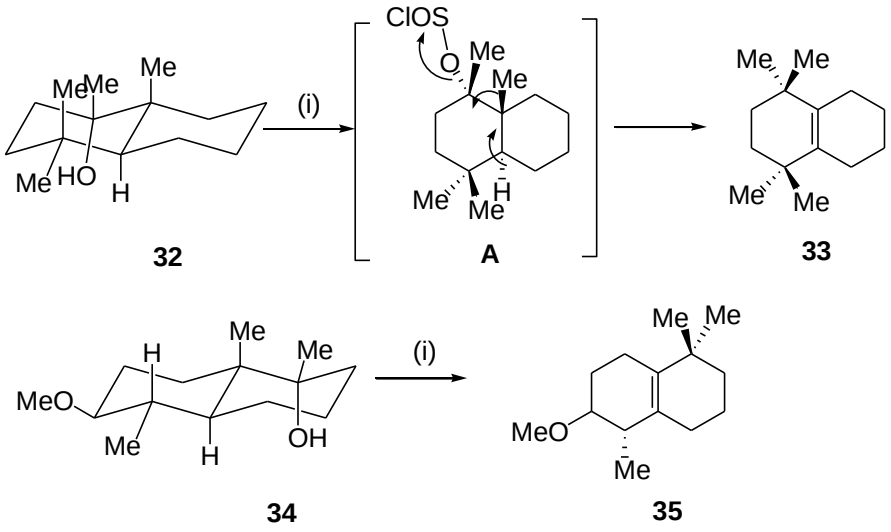
Thionyl chloride and pyridine have been extensively used for dehydration of alcohols[22,23] which undergo molecular transformation with this reagent yielding substituted alkenes and many unexpected products. Darzens[23] has reported the formation of olefin ester **27** by the dehydration of tertiary alcohol **26** with thionyl chloride and pyridine. The introduction of double bond at the adjacent position of the carbonyl group of the alcohol **28** was achieved[24] by dehydration with thionyl chloride and pyridine but Apsimon and Yamasaky[25] encountered difficulty in the dehydration of tertiary alcohol **30** to the alkene **31** (Scheme 6) employing the mentioned reagent.



Reagents: (i) $SOCl_2$, Py

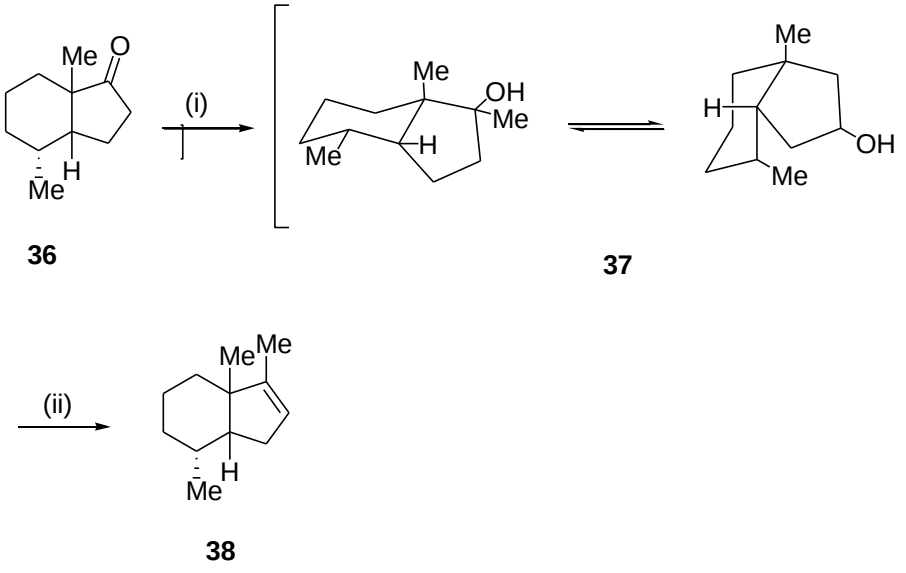
Scheme 6

A spectacular rearrangement of the tertiary alcohol[26] **32** to the tetrasubstituted alkene **33** was observed by the treatment with thionyl chloride and pyridine (Scheme 7). The transformation can be explained by assuming the formation of an intermediate **A** from which the elimination of the chlorosulfite group (OSOCl) and 1,2-methyl-group shift occurred in a concerted manner leading to the formation of cyclic alkene **33**. Similar observation[26] was also recorded by isolation of the alkene **35** during the dehydration of tertiary alcohol **34** with thionyl chloride and pyridine. We believe that the alkene **35** can be utilized for the synthesis of sesquiterpenoid compounds.



Reagents: (i) $SOCl_2$, Py

Scheme 7



Reagents: (i) MeLi, Et_2O; (ii) $SOCl_2$, Py

Scheme 8

A very interesting observation was recorded[26] during the dehydration of octahydroindenol **37**, prepared from the ketone[26] **36**. The alcohol **37** on treatment with thionyl chloride and pyridine suffered no rearrangement like the other tertiary alcohols **32** and **34** but afforded only the alkene **38** (Scheme 8) in major amount. It was very curious to find that the alcohols **32** and **34** underwent rearrangement with thionyl chloride and pyridine while under similar reaction condition alcohol **37** produced the alkene **38**. We believe that the *trans*-juncture of the alcohols **32** and **34** enable an

antiplanar arrangement of the migrating methyl group and the hydrogen at the bridgehead position, thus fulfilling the stereoelectronic requirement for a more or less synchronous elimination–rearrangement reaction. A similar orientation can not be adopted by the alcohol **37**.

The mentioned examples indicate that the thionyl chloride has played an important role in the dehydration of alcohols, thus affording the alkenes **27**, **29**, **33**, **35** and **38**. We believe that these alkenes can be utilized as starting material for the synthesis natural products and bioactive substances.

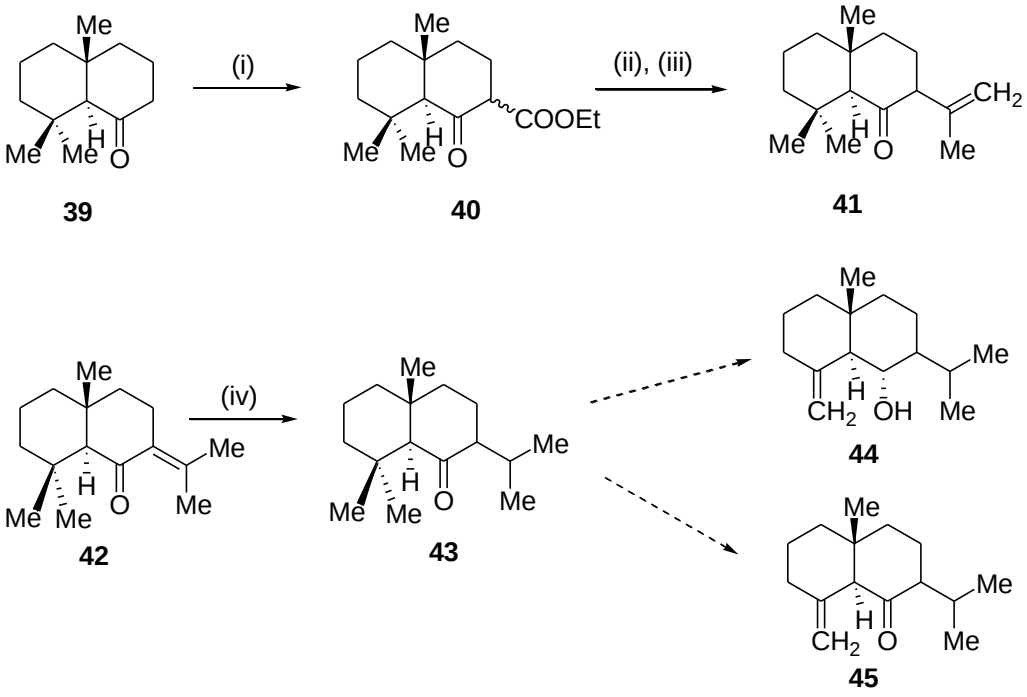
2.3. Acid catalysed (*p*-toluenesulphonic acid, sulphuric acid, hydrochloric acid) dehydration

Dehydration of alcohols catalyzed by acid especially by *p*-toluenesulphonic acid has frequently been used in our laboratory for the synthesis of alkenes. It is necessary to mention that dehydration of alcohols with *p*-toluenesulphonic acid, sulphuric acid and hydrochloric acid most often yield the desired alkene. In some occasions occurs the rearrangement of molecule. During the synthesis of terpenoid compounds the introduction of olefinic bond in the suitable position was essential. The acid catalyzed dehydration proved useful to achieve the objective. Some examples are cited below.

The ketone[27] **39** was treated with diethyl carbonate and sodium hydride in dimethoxyethane to yield β-ketoester **40** which was made to react with MeLi in ether to obtain the tertiary alcohol. Dehydration with 10% hydrochloric acid yielded the alkenes **41** and **42** in unequal proportion. The dehydration with thionyl chloride and phosphorous oxychloride was not successful. The formation of these alkenes proved useful for the synthesis of the sesquiterpenes junenol **44** and acalomone **45** because direct introduction of the isopropyl group to the ketone **39** was not successful. Hydrogenation of the mixture of these alkenes generated the isopropyl ketone **43** which was utilized[28] for the synthesis of sesquiterpenes junenol **44** and acolamone **45** (Scheme 9).

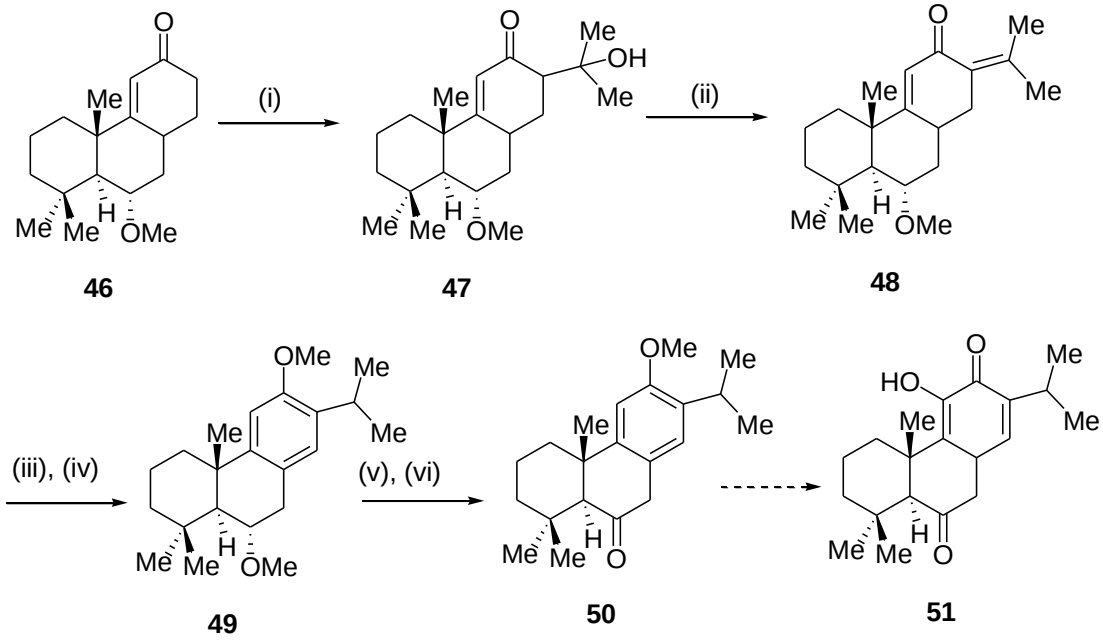
Dehydration of alcohol catalyzed by acid to obtain alkene was also attempted during the synthesis of (±)-taxodione **51** which is a diterpenoid quinone and exhibits its tumor inhibitory activity against Walker carcino sarcoma 256 in rats.

Ketone[29] **46** was converted to the alcohol **47** by treatment with acetone and lithium diisopropylamide in tetrahydrouran. Heating the alcohol **47** in benzene under reflux with a catalytic amount of *p*-toluenesulfonic acid produced the dienone **48** (Scheme 10). Due to the formation of the dienone **48**, the synthesis of taxodione **51** was achieved without any difficulty. The dienone **48** on heating with 5% sulphuric acid in methanol underwent aromatization yielding phenol which on methoxylation produced the dimethoxy compound **49**. Demethoxylation followed by oxidation and methoxylation afforded the tricyclic ketone **50** whose transformation to taxodione **51** has already been reported.[30]



Reagents: (i) $CO(COOEt)_2$, NaH; (ii) MeLi,Et_2O; (iii) 10% HCl, MeOH; (iv) PtO_2, MeOH

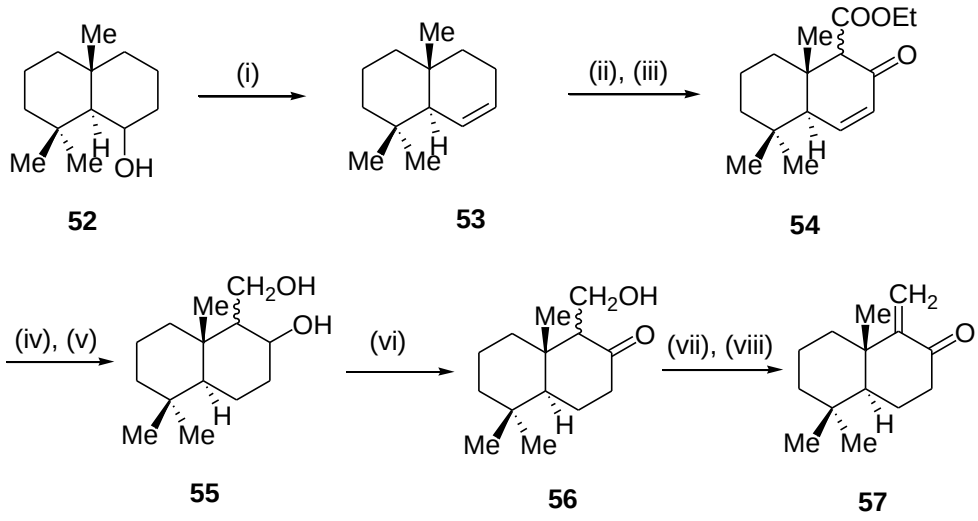
Scheme 9



Reagents: (i) LDA, $ZnCl_2$, Me_2CO; (ii) PTSA, C_6H_6; (iii) 5% H_2SO_4, MeOH; (iv) Me_2SO_4, Me_2CO, K_2CO_3; (v) Me_3SiCl, NaI, MeCN: (vi) CrO_3, H_2SO_4

Scheme 10

The utility of *p*-toluenesufonic acid in the synthesis of alkene has been recorded[31] during the synthesis of 8-methylene-4,4,8a-trimethyl-7-oxo-octahydronaphthalene **57** (Scheme 11). The alcohol[1] **52** on dehydration with *p*-toluenesulfonic acid adsorbed on silica gel afforded the alkene **53** in 97% yield. The double bond occupied the desired position and thus the synthesis of **57** was accomplished without difficulty. The alkene **53** was converted to olefin ester **54** in two steps (allylic oxidation and carboxylation). The catalytic hydrogenation and metal hydride reduction the produced the diol **55.** Selective oxidation with hypochlorite in acetic acid afforded the diol **56** whose tosyl derivative underwent smooth elimination on treatment with base furnishing the desired compound **57**, a potential intermediate for the synthesis of terpenoid compounds such as zonarol, isozonarol, 2-desoxystemodinone and the perfumery agent (+)-ambrox.



Reagents: (i) PTSA, silica gel; (ii) CrO_3, Py, 3,5dimethylpyrazole; (iii) DME, $CO(COOEt)_2$, NaH; (iv) PtO_2, MeOH; (v) $LiAlH_4$, THF; (vi) $NaClO_4$, MeCOOH, (vii) TsCl, Py; (viii) 1,5-diazabicyclo[5.4.0]-undec-5-ene

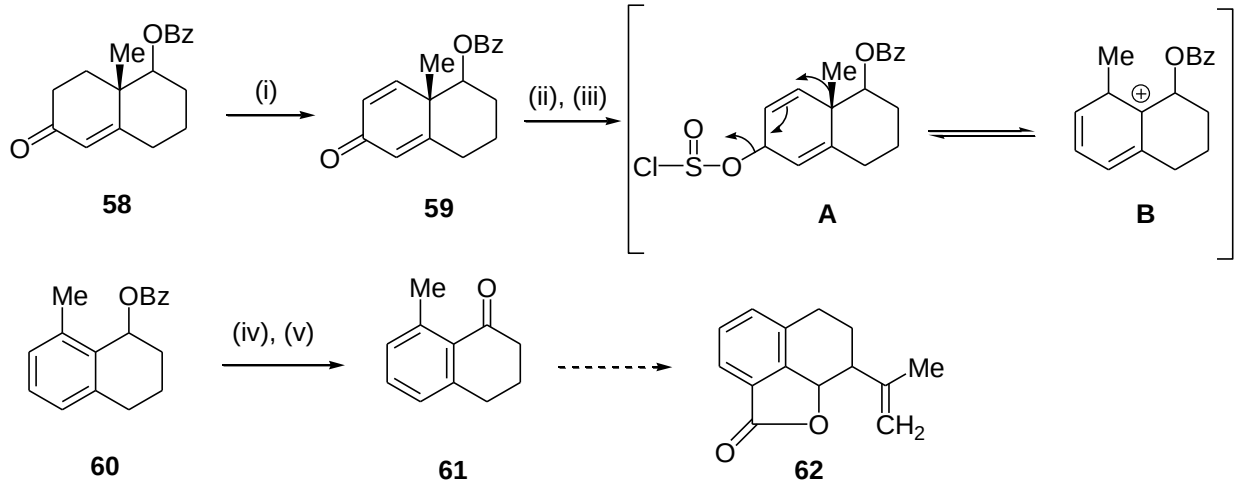
Scheme 11

The examples cited above exhibit the role of acids in conversion of the alcohols into the alkenes **41**, **42**, **48** and **53** which were utilized in the synthesis of potential intermediates for diterpene and sesquiterpene.

2.4. 2,6-Dichloro-3,5-dicyanobenzoquinone (DDQ)

2,6-dichloro-3,5-dicyanobenzoquinone (DDQ) has been employed in our laboratory for the introduction of double bond adjacent to carbonyl group. It can be seen from the examples cited below that the facile introduction of the double bond adjacent to carbonyl group was very helpful in the synthesis of decalin and phenanthrene moiety for their conversion to natural products. Some examples are given below.

Ketone **58** on heating with DDQ in dioxane yielded the dienone **59** whose transformation to the tetralin **60** was achieved by metal hydride reduction followed by treatment with thionyl chloride and pyridine. The resulting product on further reduction followed by oxidation produced the ketone[32] **61** which is a potential intermediate for the synthesis[33] of sesquiterpene platphyllide **62** (Scheme 12). The transformation of **59** can be explained by assuming the formation of the intermediate **A** whose methyl group migrated followed by the elimination of the chlorosulfite (OSOCl) leading to the formation of the intermediate **B** which rearranged to the tetralin **60**.

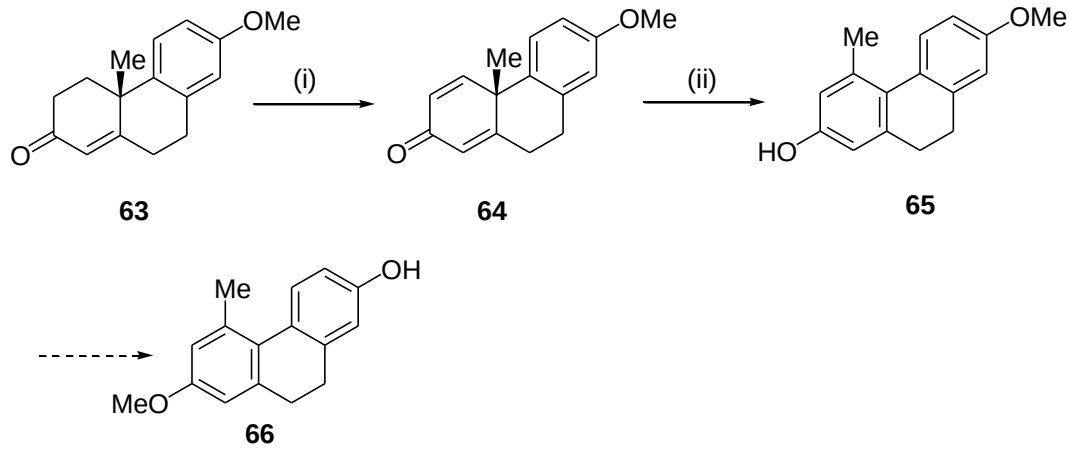


Reagents: (i) DDQ, dioxane; (ii) $NaBH_4$, MeOH; (iii) $SOCl_2$, Py; (iv) $LiAlH_4$, THF; (v) $BaMnO_4$, CH_2Cl_2

Scheme 12

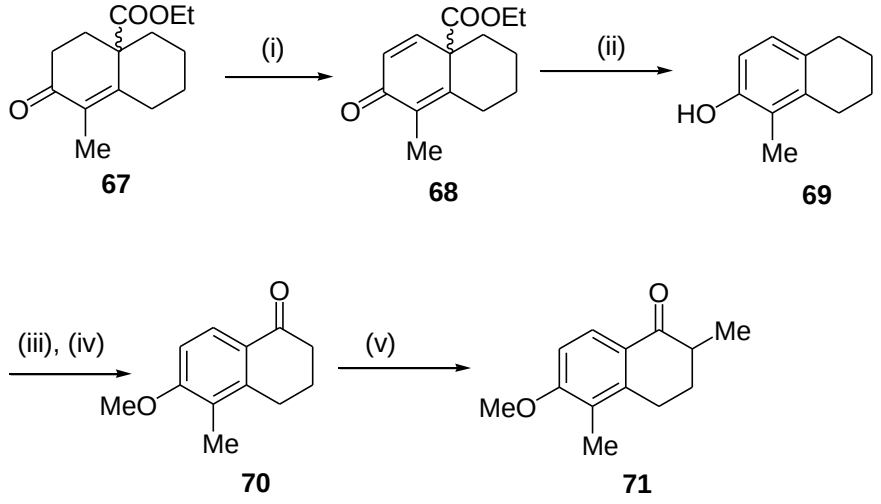
Similarly the ketone[34] **63** in dioxane on heating with DDQ yielded the dienone[35] **64** which was converted to phenol **65** by heating with acid**.** The phenol was utilized for the synthesis of phytoalexin orchinol[36] **66,** a dihydrophenanthrene and biological active natural product (Scheme 13).

Finally it is worthwhile to add another example to show the use of DDQ in dehydrogenation of organic compounds. The ketoesters[37] **67** was converted to the dienone **68** by heating with DDQ in dioxane. The dienone were subjected to hydrolysis with potassium *t*-butoxide in *t*-butanol. Decarboxylation followed by aromatization occurred in one step yielding the tetralol **69** which was methylated and oxidized to obtain the tetralone **70**. Methylation[38] of the tetralone **70** furnished the tetralone[37] **71** in good yield (Scheme 14). The tetralone **70** is an useful intermediate[39] for the construction of the fundamental skeleton of steroids and the tetralone **71** has been utilized for the synthesis[40] of cloven-3-one and epiclovene-3-one.



Reagents: (i) DDQ, dioxane; (ii) PTSA, C_6H_6

Scheme 13



Reagents: (i) DDQ, dioxane; (ii) C_4H_9OK/C_4H_9OH; (iii) Me_2SO_4, Me_2CO; (iv) CrO_3, MeCOOH; (v) Et_3B, NaH, MeI

Scheme 14

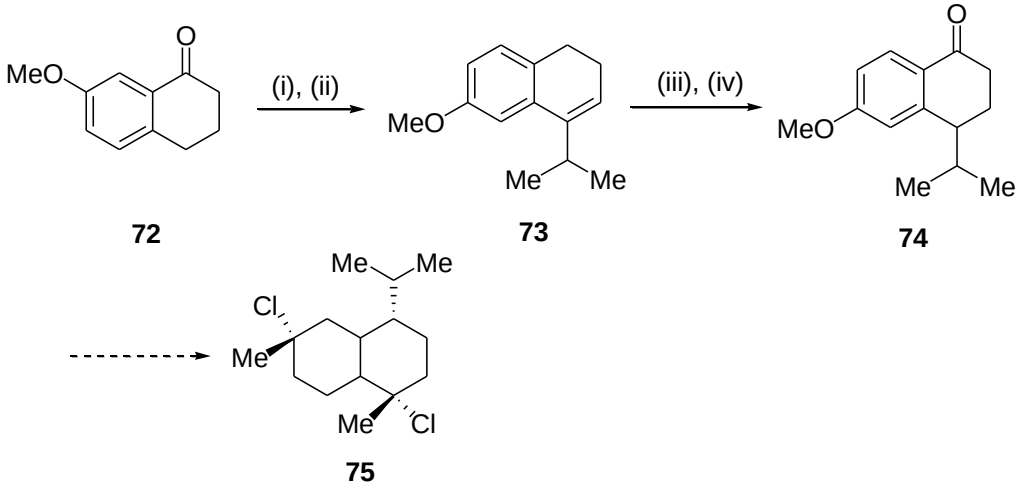
It can easily be appreciated the use of DDQ in the conversion of α,β-unsaturated ketones into the dienones and their utility in the synthesis of terpenoid compounds.

2.5. Grignard Reagents (MeMgBr, $Me_2CHMgBr$)

The chemical literature indicates that many Grignard reagents have been used the direct conversion of the carbonyl group into the alkene for their transformations into potential intermediates for the synthesis of natural products and bioactive compounds. In relation of our studies on terpenoid compounds several tetralones were made to react with Grignard reagents to yield alkenes and most

of these alkenes were utilized either for the synthesis of diterpenes and sesquiterpenes or potential intermediates for the terpenoid compounds. Some examples are cited below.

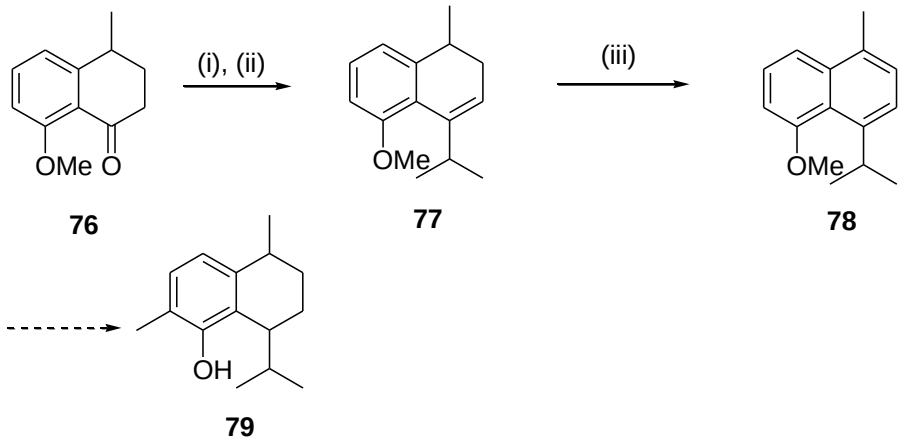
7-methoxy-1-tetralone **72** was made to react with isopropylmagnesium chloride in ether in presence of cerium chloride to obtain an alcohol, which on dehydration with *p*-toluenesulphonic acid yielded the alkene[41] **73** in high yields whose transformation into the tetralone **74** was accomplished by hydrogenation and oxidation respectively. Tetralone **74** is a potential intermediate for the sesquiterpene (±)-cadinene dihydrochloride **75** (Scheme 15).



Reagents: (i) i-PrMgCl, $CeCl_3$, THF, 0 ^oC; (ii) PTSA, C_6H_6; (iii) H_2, Pd-C 10%, 1 atm; (iv) 10% CrO_3-AcOH

Scheme 15

Similarly the tetralone **76,** on treatment with isopropylmagnesium chloride in presence of cerium chloride followed by dehydration produced the alkene **77** which on dihydrogenation afforded the substituted naphthalene **78**. The conversion of **78** into the phenolic sesquiterpene (±)-*cis*-5-hydroxycalamenene **79** was realized[42] in three steps (demethoxylation, formylation and hydrogenation) (Scheme 16). The sesquitepene **79** possess antioxidant, antimicrobial and antifungal activity.

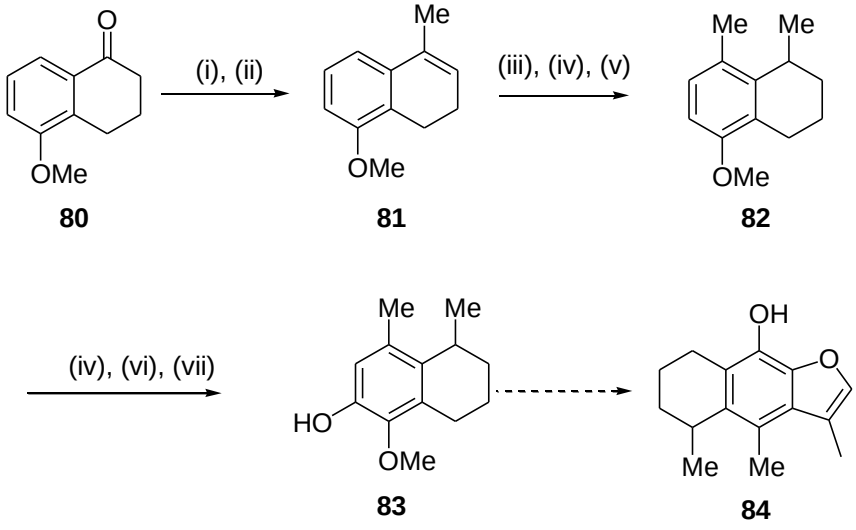


76 **77** **78** **79**

Reagents: (i) *i*-PrMgCl, THF, 0 ^{0}C; (ii) HCl, 6N; (iii) DDQ, CH_2Cl_2

Scheme 16

5-Methoxy-1-tetralone **80** was converted to the alkene **81** by the mentioned procedure. The alkene **81** was subjected to hydrogenation, bromination, metalation and methylation respectively to obtain the methyltetralin **82**. Its conversion to the tetraol **83** (Scheme 17) was accomplished in three steps (bromination, formylation and oxidative rearrangement).[43] The three steps conversion of tetraol into the sesquiterpene (±)-cacalol **84** has already been accomplished[44] employing standard organic reactions. Thus the alkene **81** can be considered as potential intermediate for the synthesis de cacalol **84** whose biological activities are well documented.[44]

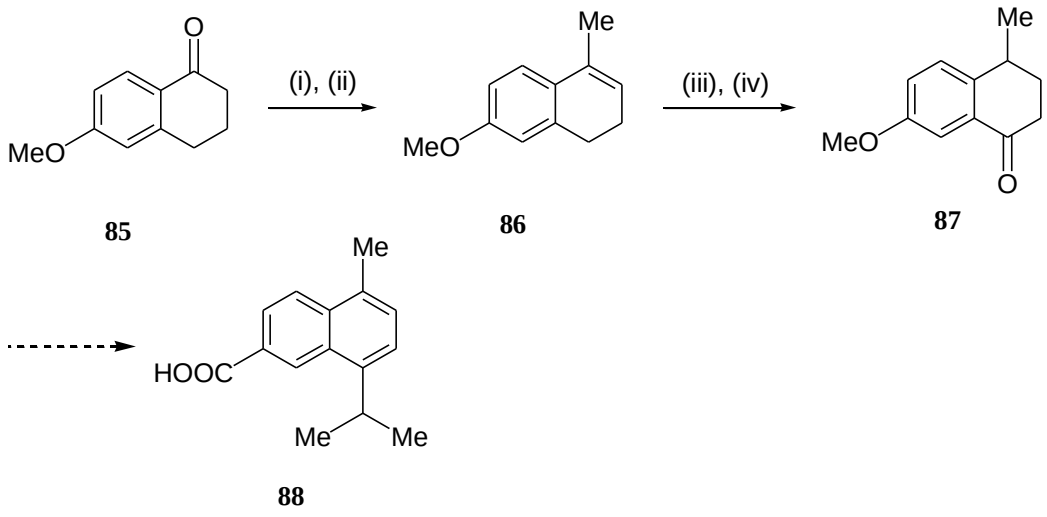


80 **81** **82** **83** **84**

Reagents: (i) MeMgBr, Et_2O; (ii) HCl, 6N; (iii) H_2, Pd/C, EtOH; (iv) NH_4Br, H_2O_2, AcOH; (v) n-BuLi, MeI; (vi) DMF, n-BuLi; (vii) H_2O_2, H_2SO_4, MeOH

Scheme 17

6-Methoxy-1-tetralone **85** was converted by the mentioned Grignard reagent to the alkene **86.** Its conversion into the tetralone **87** was effected by catalytic hydrogenation and oxidation respectively. Tetralone **87** served as potential intermediate for the synthesis[45] of cadalen-15-oic acid **88** (Scheme 18), a sesquiterpene that exhibits anti-inflamatory and analgesic activity.



Reagents: (i) MeMgBr; (ii) HCl, 6N; (iii) H_2, Pd/ C(10%); (iv) 10% CrO_3 - CH_3CO_2H

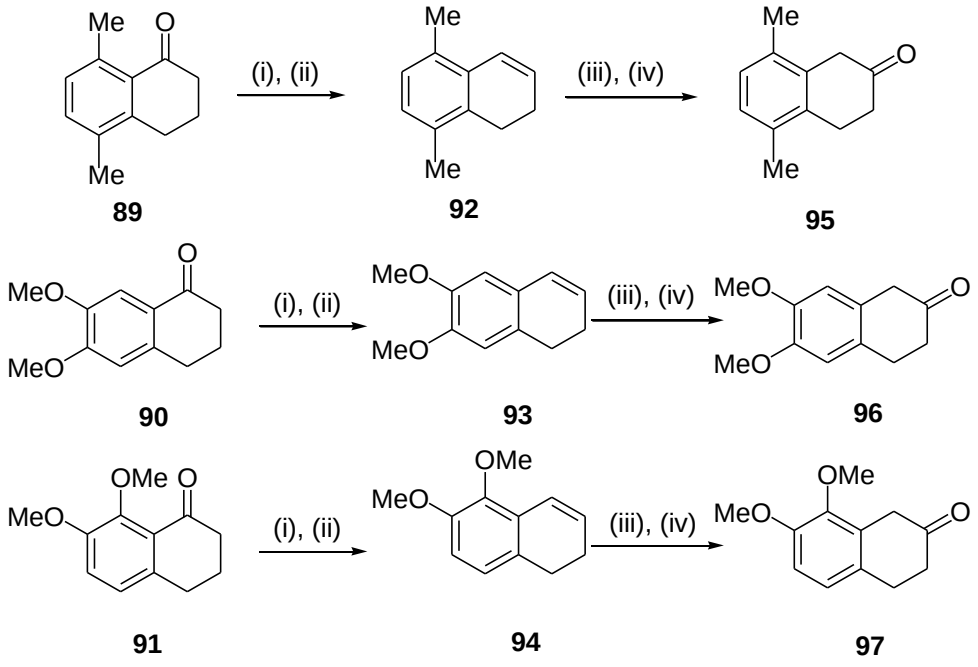
Scheme 18

The importance of Grignard reagents in the synthesis of the alkenes **73**, **77**, **81** and **86**, from the tetralones can be observed from the mentioned examples. These alkenes proved useful for the synthesis of bioactive sesquiterpenes.

2.6. 2,4-Pentanediol and *p*-toluenesulfonic acid

It was reported by Vuligonda and collaborators[46] that 1-tetralones on heating with 2,4-pentanediol and *p*-toluenesulfonic acid are converted to dihydronaphthalenes. We have observed this method worked successfully with some substituted 1-tetralones, prepared in our laboratory. The dihydronaphthalenes were obtained in high yield. Thus the tetralones **89-91** were converted to dihydronaphthalenes[47-49] **92-94** respectively in good yield (Scheme 19). These naphthalenes on epoxidation and acid hydrolysis afforded tetralones **95-97** respectively.

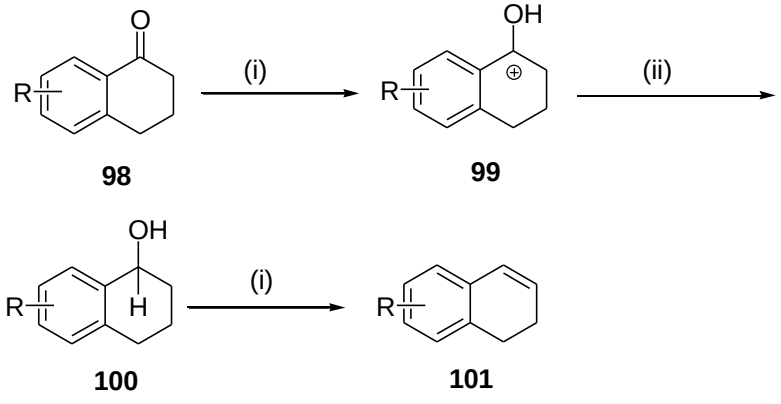
The tetralone **95** is an attractive intermediate for the synthesis of occidol[50] and emmotin–G methyl ether[51].Tetralone **96** has been used as starting material for many dopaminergic compounds. Its utility has been recorded in the synthesis of natural alkaloids, cyclic amino acids and as novel antagonists of human TRPVT. The tetralone **97** is an intermediate in the synthesis of analgesics, morphines and steroids. These tetralones were obtained very easily and in high yield due to one step deoxygenation procedure with 2,4-pentanediol and *p*-toluenesulphonic acid.



Reagents: (i) 2,4-pentanediol; (ii) PTSA, Toluene, reflux; (iii) MCPBA, CH_2Cl_2; (iv) H_2SO_4 dil, EtOH, reflux

Scheme 19

A possible mechanism for the formation of the alkene from tetralone is depicted in Scheme 20. The *p*-toluenesulphonic acid forms the carbocation **99** from the tetralone **98**. The carbocation **99** is converted to the benzylic alcohol **100** due to the migration of the hydride anion from the 2,4-pentanediol. The alcohol **100** undergoes dehydration to the alkene **101**.



Reagents:(i) PTSA, Toluene, reflux; (ii) 2,4-pentanediol

Scheme 20

3. Conclusions

The present review summarizes the results of our investigation concerning the transformation of carbonyl compounds, mostly decalones and tetralones, into the alkenes using several reagents. The resulting olefinic compounds were utilized for the synthesis of natural products and bioactive compounds. We have shown the importance of several reagents in the conversion of carbonyl compound into the alkene. We hope in near future more reagents will be utilized for the transformation of the carbonyl group into the alkene.

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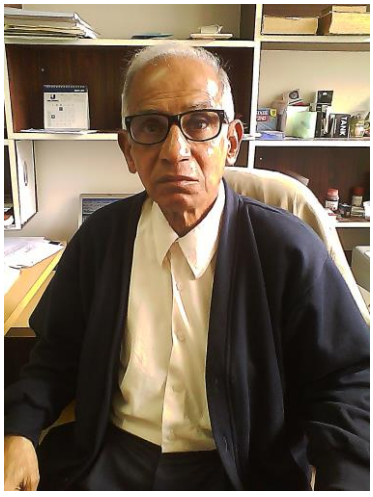

Ajoy K. Banerjee, who received D.Phil degree 1965 from the University of Kolkata (India), joined at IVIC in 1968. Since 1982 till now he is working as senior research scientist. Most of his works are related to synthetic studies on terpenoid compounds (diterpenes and sesquitepenes). He teaches organic chemistry (mainly reaction mechanism and molecular rearrangements) to the students who join IVIC for M.Sc or Ph.D degree. Dr. Banerjee is the author of two books on organic chemistry written in Spanish language.

Elvia V. Cabrera is associate professor of organic chemistry at the University of Zulia, Maracaibo, Venezuela. In 2012, Dr. Cabrera received her Ph. D. in organic chemistry from University of Zulia. Her research work is related to the synthesis of natural products related to sesquiterpenes.

