CHAPTER - V

Synthesis and characterization of certain Allylation and N-tert-butyloxycarbonylation (N-Boc) reactions using eco friendly catalysts.
Synthesis and characterization certain Allylation and N-tert-butyloxycarbonylation (N-Boc) reactions using ecofriendly catalysts

5.1. Introduction:
Carbon-Carbon bond construction in general is the basis for all of organic chemistry. The formation of carbon–carbon single bonds is of fundamental importance in organic synthesis. As a result, there are an ever-growing number of methods available for carbon–carbon bond formation. The most important carbon–carbon bond formation reactions include the aldol reaction, Reformatsky reaction, Claisen rearrangements, Friedel- Crafts reaction, Grignard reaction, Diels-Alder reaction, Wittig reaction, Heck reaction, Suzuki coupling, Grubb’s ring closing metathesis, and so forth. Many of the most useful procedures involve the addition of organometallic species or enolates to electrophiles, as in the Grignard reaction, the aldol reaction, the Michael reaction, alkylation reactions and coupling reactions. Significant advances in both main-group and transition-metal-mediated carbon–carbon bond-forming reactions have been made over the past decade. In one of the recent reports [1], Taber highlighted important methods for the construction of a single, double, and triple bonds. Carbon-carbon bond formation through organometallic elimination reactions has been reviewed by several investigators from time to time [2-6].

On the other hand, the development of mild and selective methods for protection and deprotection of functional groups continue to be one of the most important tools in synthetic organic chemistry [7]. Quite often the desired reaction is accompanied by side reaction(s) at other parts of the molecule, especially when more than one functional group is present. Functional groups are usually the most reactive sites in the molecule, and the side reactions encountered due to these functional groups might hamper the progress of desired reaction. Therefore, there is a need to make inert the unwanted functional group and evaluate the synthesis at each step to understand the insight of these side reactions. Such understanding is acquired through experience and knowledge of reaction mechanism, variations in structure effect on chemical reactivity and reaction stereochemistry. Thus the use of protecting groups has become stimulus to eliminate or
suppress the unwanted side reactions in organic synthesis. The tert-butyloxy carbonyl (Boc) is still one of the most widely used in organic chemistry, used to protect primary or secondary amines as well as amino acids in peptides chemistry [8-10]. In view of these reasons, the author has tried two diversified, useful synthetic protocols Viz., (i) to introduce a new set of C-C bond formation reactions using tetrabutylammonium fluoride (TBAF) as an efficient catalyst for allylation of aldehydes with allyltrimethylsilane, and (ii) Zinc mont as an efficient catalyst for N-tert-butyloxycarbonylation (N-Boc) reactions for the protection of amine 3,5 Dichloro aniline.

5.2. Section A: Tetrabutylammonium fluoride as an efficient catalyst for allylation of aldehydes with allytrimethyl silane: The allylation of carbonyl compound is one of the most important C-C bond formation reactions. The Lewis acid promoted allylation of aldehydes has become an important carbon–carbon bond forming reaction in organic chemistry [11-14]. Lewis acid promoted allylation of aldehydes has become an important carbon–carbon bond forming reaction in organic chemistry. In this context, Bartoli et al [15] accomplished an alternative over existing catalytic processes, wherein aldehydes are subject in acetonitrile to reaction of allylation with allyltributylstannane in the presence of cerium(III) chloride heptahydrate (CeCl₃·7H₂O), an inexpensive and mild Lewis acid. The allylation has been accelerated by using an inorganic iodide as a cocatalyst, and various iodide salts were examined. The procedure must use allylstannane reagent instead of allylsilane reagent, desirable for environmental reasons, but high chemoselectivity was observed, and this is opposite the results obtained with other classical Lewis acids such as TiCl₄ and Et₂O.BF₃. From the same school Bartoli et al developed cerium (III) chloride heptahydrate/sodium iodide complex (CeCl₃·7H₂O/NaI) as a useful promoter in the carbon-carbon bond forming reaction by addition of allyltributylstannanes to aldehydes. The reaction of 2-butenyltributylstannane showed that the regio- and the stereochemical outcomes depend on the reaction conditions. When the promoter is adsorbed on a solid support (aluminum oxide), a highly prevalent formation of the γ-adduct is observed in solvent-free conditions. Conversely, when the reaction is carried out in acetonitrile as the solvent, α-adduct largely prevails. In the last case, a complete stereo control is observed, the less stable (Z)-isomer being obtained in high geometrical purity [16]. However, not much work appeared on the use of allylsilane compounds in these protocols [17, 18]. The
reaction of allylsilane with a carbonyl compound in presence of Lewis acid or fluoride ions is known as the Sakurai-Hosomi reaction, which has been extensively studied and applied successfully in organic synthesis [19]. Activation by Lewis acids is critical for an efficient allylation to take place. Allylation of aldehydes by various allylic metals is an important synthetic transformation [19] as the resultant homoallylic alcohols are versatile synthons in the preparation of materials, natural products, bioactive compounds and many complex molecules [20 - 22]. The general practice for preparation of homoallylic alcohols is carried out by nucleophilic addition of allylic metal reagent to carbonyl compounds. Previously numerous reports on such transformation was carried out using various Lewis, Bronsted acid [23-27], metal salts [28], β-cyclodextrine [29], organometallic reagents in organic media, aqueous media, ionic liquids[30] and PEG[31]. Development of more improved synthetic methods for the preparation of homoallylic alcohols remains an active research area. Tetrabutylammonium fluoride has been used widely as a reagent in organic chemistry for the efficient cleavage of various silyl protecting groups from O-silylated nucleosides [32], and pyrophosphates [33]. It is also used as an efferent reagent in many fluoride-assisted reactions such as deprotection of silyl ethers [34], acetals[35], esters[36] carbamates,[37] and N-sulfonyl groups [38] as well as desilylation [39] and fluorination[40]. TBAF is also used as a mild base in a variety of base-catalyzed reactions such as aldol-type condensation reactions [41], Michael-type reactions[42], dehydrohalogenation of alkyl halides to alkenes [43]. It is also used an efficient catalyst for [2 + 3] cycloaddition reactions [44]. Indium mediated allylations are very selective, offering four different types of selectivity: chemoselectivity, regioselectivity, diastereoselectivity, and enantioselectivity. Indium mediates the allylation of a wide variety of electrophiles [45] The examples in the following scheme illustrate the breadth of applications of IMA.
This part of the study reports the reaction of allyltrimethylsilane 1 with aldimesines 2 in the presence of tetra-n-butylammonium fluoride to give the corresponding homoallylamines 3 in moderate to excellent yields. The allylation mechanism of imines as well as that of aldehydes can be reasonably interpreted by a fluoride-triggered autocatalytic procedure. We here in report a convenient method involving the use of tetrabutylammonium salt (TBAF), as a environmentally safe organic catalysts for synthesis of homoallylic alcohols (Scheme 1).

Scheme 1: Allylation of aldehydes catalyzed by TBAF

To identify the best catalytic system, various reaction parameters were screened in the allylation reaction between benzaldehyde and allyltrimethylsilane and the results are compiled in Table - 1.
Table-1: Screening of reaction parameters for the synthesis of 1-(phenyl)-3-buten-1-ol

| Entry | Solvent | Catalyst | Yield [%]  
<table>
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<tr>
<td>1</td>
<td>DMSO</td>
<td>TBAF</td>
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<tr>
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<td>3</td>
<td>THF</td>
<td>TBAF</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>Acetonitrile</td>
<td>TBAF</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>1,4-Dioxane</td>
<td>TBAF</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>DMSO</td>
<td>TBAB</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>DMSO</td>
<td>TBAF</td>
<td>–</td>
</tr>
</tbody>
</table>

a Reaction conditions: benzaldehyde (1 mmol), allyltrimethyl silane (1.2 mmol), catalyst (0.1 mmol), solvent (3 mL), reaction time (5 h), room temperature; b Isolated yields.; c Allytributyl tin was used as allylating agent instead of allyltrimethyl silane.

Out of the screened solvents, DMSO proved to be the best solvent. It is important to note that the reaction did not proceed even under drastic conditions when the reaction is conducted with tetrabutylammonium bromide (TBAB) as catalyst using allyltrimethyl silane as allylating agent or TBAF as a catalyst using allytributyl tin as allylating agent (Table 1, entry 6, 7). A control reaction conducted under identical conditions devoid of TBAF gave no coupled product despite prolong reaction time. The author chose a variety of structurally divergent aldehydes possessing a wide range of functional groups for our study to understand the scope and the generality of the TBAF catalyzed allylation of aldehydes and the results are summarized in table- 2. 2. Among the various aldehydes tested, heteroaromatic aldehydes such as 4-pyridinecarboxaldehyde, 3- pyridine carboxaldehyde, 2-pyridinecarboxaldehyde and 2-furaldehyde (Table 2, entries 8-11), gave excellent good yields of the corresponding homoallylic products with short reactions time. Among the various aromatic aldehydes tested, the rate of the reaction is faster with benzaldehydes having electron-withdrawing groups such as 4-nitrobenzaldehyde, 2-chlorbenzaldehyde and 4-chlorobenzaldehyde (Table 2, entries 2-4)
compared to the substrates bearing an electron-donating group such as \( p \)-anisaldehyde, 4-\textit{tert}-butylbenzaldehyde and 3,4,5-trimethoxybenzaldehyde (Table 2, entries 5-7). Highly conjugated aromatics like cinnamaldehyde and aliphatic aldehydes such as cyclohexylcarboxaldehyde afforded moderate yields of corresponding homoallylic alcohols. Bicyclic aromatic aldehyde such as 1-naphthaldehyde was also efficiently converted into corresponding homoallylic alcohols with good yields. Nevertheless, the TBAF catalyzed allylation does not work efficiently for ketones.

5.2.1. A typical procedure for allylation of benzaldehyde with allyltrimethyl silane:

TBAF (0.1 mmol) was added to a mixture of benzaldehyde (1 mmol) and allyltrimethyl silane (1.2 mmol) in DMSO (3 mL) the mixture was stirred for an appropriate time at room temperature. After completion of the reaction, as indicated by TLC, the reaction mixture was quenched with aqueous sodium hydrogen carbonate and was extracted with ethyl acetate (3×10 mL). The combined organic extracts were dried over anhydrous sodium sulfate and filtered. Solvent was evaporated under reduced pressure and concentrated \textit{in vacuo} to give the crude product. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate, 90:10) to afford pure 1-(phenyl)-3-buten-1-ol.
Table-5.2.2: Allylation of aldehydes catalyzed by TBAF

<table>
<thead>
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<th>Entry</th>
<th>Substrate (R-cho)</th>
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<th>Yield (%)</th>
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Section B: Zinc mont an efficient catalyst for N-tert-butyloxy carbonylation (N-Boc) reactions for protection for Amines:

The increasing demand for cleaner processes promoted by stringent environment laws requires use of eco-friendly and selective catalysts. Use of inexpensive and non-polluting reagents is highly desirable in recent years and the use of clays as catalyst supports has received considerable attention. Academic and industrial interest has focused on the use of acid activated montmorillonite K10-supported zinc chloride (zinc montmorillonite, Zn2+-mont); use of this remarkable material has been first reported in 1989[46].

Montmorillonites are layered clay minerals, composed of alumina octahedral sheets sandwiched by two silica tetrahedral layers. The aluminum atoms in the center of the octahedral sheets are partly replaced by magnesium or iron atoms, resulting in cation deficiency over the whole clay. To compensate for the cationic deficiency, some cations, typically sodium ions, are present in the expansive interlamellar spaces between two-dimensional silicate sheets. Various types of metal cations and protons can be readily introduced into the interlayer spaces of the mont via cation exchange with the sodium, thus creating the acidic nature. The metal-cation exchanged montmorillonite catalysts (Mn+-monts), exhibited excellent catalytic performance in various organic transformations.

Preparation of Metal Ion–Exchanged Montmorillonites:

Al-Mont, Sc-Mont, Ti-Mont, Fe-Mont, Ni-Mont, Cu-Mont, Zn-Mont, Ga-Mont, Zr-Mont, Sn-Mont, La-Mont and Sm-Mont were prepared from Na-Mont (cation-exchange capacity = 1.19 mequiv g⁻¹) by cation-exchange using aqueous solutions of corresponding salts, such as Al(NO₃)₃.9H₂O, Sc(NO₃)₃.4H₂O, Ti(Oi-Pr)₄ in aqueous hydrochloric acid, Fe(NO₃)₃.9H₂O, Ni(NO₃)₂.6H₂O, Cu(NO₃)₂.3H₂O, Zn(NO₃)₂.6H₂O, Ga(NO₃)₃.8H₂O, ZrCl₄, SnCl₄.5H₂O, La(NO₃)₃.6H₂O, and Sm(NO₃)₃.6H₂O. A typical procedure is described below.

A typical procedure is described below.

To a solution of Zn(NO₃)₂.6H₂O (100 g, 0.24 mol) in deionized water (800ml) was added Na-Mont (cation-exchange capacity = 1.19 mequiv g⁻¹) (100 g). The mixture was stirred vigorously at room temperature for 16 hours. The resultant suspension was filtered on a Buchner funnel by suction. The clay was collected suspended again in deionized water
(400 mL) with stirring at room temperature for 16 hours, filtered on a suction funnel, and washed with deionized water (200 ml). The precipitate was again suspended in deionized water (400 ml) with stirring at room temperature for 14 hours, filtered on a suction funnel, and washed with deionized water (200 ml). The precipitate was suspended again in a mixture of deionized water (200 ml) and methanol (200 ml) with stirring at room temperature for 8 hours and filtered. The collected clay was dried at 100°C for 6 hours and ground to pass through a 60 mesh screen. The powdery clay was dried at vacuum at 100°C for 4 hours to give Zn-Mont as an off-white solid (88 g).

The introduction and removal of protecting groups has great significance in organic synthesis. A protecting group or protective group is introduced into a molecule by chemical modification of a functional group to obtain chemoselectivity in a subsequent chemical reaction. It plays an important role in multistep organic synthesis [47]. In many preparations of delicate organic compounds, some specific parts of their molecules cannot survive the required reagents or chemical environments. Then, these parts, or groups, must be protected. The development of protecting groups and the study of its consequent deprotection is a field of interest, often unavoidable need in the synthesis of complex molecular structures. The tert-butyloxycarbonyl (Boc) is still one of the most widely used in organic chemistry, used to protect primary or secondary amines as well as amino acids in peptides chemistry [48]. Protecting groups are more commonly used in small-scale laboratory work and initial development than in industrial production processes because their use adds additional steps and material costs to the process. However, the availability of a cheap chiral building block can overcome these additional costs.

The tert-butyloxycarbonyl group (BOC group) is a protecting group used in organic synthesis. The BOC group can be added to the amine under aqueous conditions using di-tert-butyl dicarbonate in the presence of a base such as sodium bicarbonate. Protection of the amine can also be accomplished in acetonitrile solution using 4-dimethylaminopyridine (DMAP) as the base. Removal of the BOC in amino acids can be accomplished with strong acids such as trifluoroacetic acid neat or in dichloromethane, or with HCl in methanol [49-51]. A complication may be the tendency of the t-butyl cation intermediate to alkylate other nucleophiles; scavengers such as anisole or thioanisole may
be used [51, 52]. Selective cleavage of the N-Boc group in the presence of other protecting groups is possible when using AlCl₃. The formation of Boc-protected amines and amino acids is conducted under either aqueous or anhydrous conditions, by reaction with a base and the anhydride Boc₂O. Active esters and other derivatives such as Boc-ONH₂ and Boc-N₃ can also be used.

\[
\begin{align*}
\text{R}^\text{NH}_2 + \text{Boc}_2\text{O} & \rightarrow \text{R}^\text{NH}_2 \\
\text{NaHCO}_3 & \rightarrow \text{HCl} \\
\text{H}_2\text{O, THF} & \rightarrow \text{dioxane}
\end{align*}
\]

The Boc group is stable towards most nucleophiles and bases. In recent past several protocols were reported in which, tert-butyloxycarbonyl group (BOC group) has been used for protection amines [53-69]. At the same time few protocols were directed towards deprotection [70- 77]. However, there are some interesting studies in which Boc-protected Amines were to other functional groups [78- 86]. Thus the development of a simple and effective method, using an environmentally friendly approach as well as an economical process is in great demand in protective group chemistry. Recently from our laboratory, Rajanna and Tasneem reported Ferric Chloride as an efficient catalyst for facile BOC protection of amines [87]. In this part of the work, Zinc mont is used as an efficient catalyst for N-tert-butyloxycarbonylation (N-Boc) reactions for protection of amine 3, 5- dichloroaniline. Nevertheless, Arifuddin et. al [88] recently reported that amines are efficiently protected as their BOC derivatives under mild reaction conditions when reacted with BOC anhydride in presence of ZnCl₂.

The author chose a variety of structurally divergent amines possessing a wide range of functional groups for our study to understand the scope and the generality of the Zinc mont catalyzed N-tert-butyloxycarbonylation (N-Boc) reactions and the results are summarized in table- 2.3.

\[
\text{R}^\text{NH}_2 \xrightarrow{(\text{BOC})_2, \text{Zn mont, CH}_2\text{Cl}_2, \text{R.T.}} \text{R}^\text{NHBOC}
\]

\[\text{R}= \text{aryl, alkyl}\]

The reactions underwent smoothly in dichloromethane (DCM) within 20 to 45 min affording high product yields ranging from 80 to 96 percent depending on the nature of substrate used. N-tert-butyloxycarbonylation (N-Boc) reactions with aromatic amines
such as 3, 5 dichloro aniline, 2, 3 dichloroaniline and 2-hydroxy aniline ortho and substituted electron withdrawing groups (entries 5,8,9) are relatively slower than corresponding para compounds (entry 2). Further, the reaction times of aromatic amines with electron donating groups (entries 2, 4, 6,7 ), are less than their counter parts (entries 2, 8, 9), indicating that zinc mont catalysed N-tert-butyloxy carbonylation (N-Boc) reactions are chemo selective, keeping up with standard literature reports.

5.3.1. Typical procedure for Boc-protection of 3, 5 Dichloro aniline: A mixture of amine (1.0 mmol) and (BOC)₂O (2.0 mmol) in Zinc mont (10 mg) was vigorously stirred in dichloromethane at room temperature for the appropriate time (Table 5.3). Progress of the reaction was monitored by TLC till the completion of entire reaction (i.e. total disappearance of the amine spot then filtered the reaction mass Zinc mont is recovered. When organic layer was dried and concentrated under reduced pressure to give a crude product, which was purified by silica-gel column chromatography to afford the corresponding N-tert-butyl-carbamate. Recovered Zinc mont from the organic layer reused without loss of activity. ¹H NMR (400 MHz, CDCl₃) δ 1.51 (s, 9H), 6.81 (br s, 1H), 7.04 (m, 1H), 7.32 (d, J = 1.75 Hz, 2H).
Table-5.3: Zinc mont as an efficient catalyst for BOC formation reactions

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5.4. Conclusion

In conclusion, the author has developed a simple and efficient method for preparation of homoallylic alcohols from aldehydes and allyltrimethyl silane using tetrabutylammonium fluoride (TBAF) is an efficient organic catalyst in DMSO at room temperature. The reactions with various structurally divergent aldehydes and allyltrimethylsilane afforded moderate to excellent yields (60-96%) of products. This catalyst offers several advantages including mild reaction conditions, shorter reaction times, and good yields of products with low catalytic loading.

On the other hand, N-tert-butyloxycarbonylation (N-Boc) reactions with aromatic amines such as 3,5 dichloro aniline, 2,3 dichloroaniline, and 4-hydroxy aniline and substituted electron withdrawing groups (entries 5,8,9) are relatively slower than corresponding para compounds (entry 2). Further, the reaction times of aromatic amines with electron donating groups (entries 2, 4, 6, 7), are less than their counter parts (entries 2, 5, 8, 9), indicating that zinc mont catalysed N-tert-butyloxy carbonylation (N-Boc) reactions are chemo selective, keeping up with standard literature reports. However, in general the reactions underwent smoothly at room temperature in dichloromethane (DCM) within 20 to 45 min affording high product yields ranging from 80 to 96 percent depending on the nature of substrate used.

References:


45. (a) Frimpong, K; Wzorek, J; Lawlor, C; Spencer, K; Mitzel. T. J. Org. Chem. 2009, 74, 5861.;(b) Law, M. C; Cheung, T. W; Wong, K. Y; Chan, T. H. J. Org. Chem. 2007, 72, 923.


Mass spectrum of 1-tert-butyl 4-ethyl piperidine-1,4-dicarboxylate
IR Spectrum of tert-butyl 4-propionylpiperidine-1-carboxylate
1 H NMR Spectrum of tert-butyl (3,5-dichlorophenyl)carbamate
Mass spectrum of tert-butyl (3,5-dichlorophenyl)carbamate
IR Spectrum of tert-butyl (3,5-dichlorophenyl)carbamate
$^1$H NMR spectrum of tert-butyl (4-hydroxyphenyl)carbamate
Mass spectrum of tert-butyl (4-hydroxyphenyl)carbamate
1H NMR spectrum of 1-phenylbut-3-en-1-ol
1H NMR spectrum of 1-(4-chlorophenyl)but-3-en-1-ol
$^{1}H$ NMR spectrum of 1-(4-nitrophenyl)but-3-en-1-ol