

Recent Applications of Niobium Catalysts in Organic Synthesis

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Abstract: Niobium catalysts generally possess a good Lewis acidity and have received increased attention in recent years. The applications of niobium pentachloride as Lewis acid in organic synthesis have been recently reviewed. Since then, there has been an increasing number of examples on the use of niobium catalysts in organic reactions such as Biginelli reactions, Friedel-Crafts acylation and Sakurai-Hosomi reactions of acetals, Knoevenagel condensation, acetylation of alcohols and phenols, among others. Also, chiral niobium complexes have been reported to give high enantiomeric excesses in asymmetric Mannich-type reactions.

In this review, recent applications of these versatile reagents in organic synthesis, including our own results, will be disclosed.

Keywords: Niobium pentachloride, niobium catalysts, organic synthesis.

INTRODUCTION

Niobium lies below vanadium and above tantalum in group 5 of the periodic table. Its chemistry resembles those of tantalum and titanium being highly oxophilic. The most common niobium compound is undoubtedly niobium pentachloride (NbCl_5) which possesses a high Lewis acidity and, for this reason, has received increasing attention in recent years.

Although there are some reports on the use of NbCl_5 in organic reactions in the 1980's and 1990's, in fact few attempts had been made to popularize its use in organic synthesis until our first publications regarding the allylation of aldehydes and imines mediated by NbCl_5 , in 2001 and 2002, respectively [1]. Other works immediately followed including intramolecular ene reactions [2], nucleophilic additions to cyclic *N*-acyliminium ions [3], and aldol reactions [4].

In this meantime, many research groups around the world, especially in China, India, Japan and Brazil, started to work with this interesting and versatile Lewis acid applied to organic reactions, mainly in the last 2 or 3 years.

Some important characteristics of NbCl_5 prompted us to investigate its use as Lewis acid and will be discussed briefly. First of all, niobium compounds, especially NbCl_5 and Nb_2O_5 , are highly available in Brazil, which possesses 86% of the world reserves of niobium. Also important, it is cheaper than other commonly used Lewis acid such as InCl_3 and metal triflates (Aldrich® catalog). Finally, although a hygroscopic solid, if handled and stored properly can be used without the need of purification.

The applications of NbCl_5 in organic synthesis and the perspectives for this promising reagent have been recently reviewed [5]. Interestingly, several reactions mediated by

NbCl_5 had a different outcome as compared to the same reactions realized with other Lewis acids. The main purpose of this article is to highlight the most recent applications of niobium pentachloride and other niobium catalysts in organic synthesis, which were not disclosed in our first review, including our own recent results on this topic.

APPLICATIONS OF NIOBIUM CATALYSTS IN ORGANIC SYNTHESIS

1. Nucleophilic Additions to an Enantiopure Cyclic *N*-Acyliminium Ion

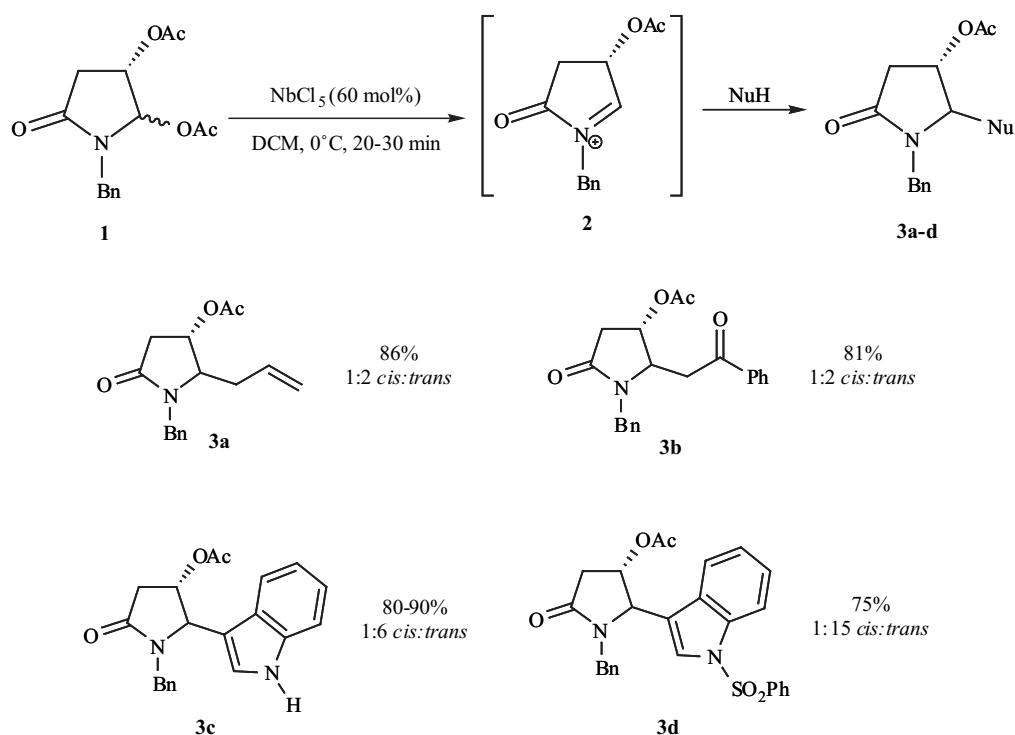
Andrade and co-workers reported the efficiency of NbCl_5 to promote the generation of an enantiopure *N*-acyliminium ion, derived from (*S*)-malic acid, and subsequent additions of carbon nucleophiles [6].

It was found that substoichiometric amounts of NbCl_5 (0.6 equivalent) were enough to transform the precursor **1** into the *N*-acyliminium ion **2**, at 0°C (Scheme 1). Several carbon nucleophiles such as allyltrimethylsilane, the silyl enol ether of acetophenone and indoles were used to attack the *N*-acyliminium ion generated and the corresponding products were isolated in good yields with low to high diastereoselectivity favoring the *trans* isomer. The low diastereoselectivity obtained for compound **3b** was unexpected in view of the better results with other Lewis acids such as InCl_3 (10:1) [7].

The *trans* diastereoselectivity obtained was explained by the preferential approach of the nucleophile to the opposite face of the acetoxy group in the cyclic *N*-acyliminium ion [7].

Noteworthy are the good results obtained in the addition of *N*-sulfonyl indole, which is less reactive than the other nucleophiles used. The corresponding product was isolated in 75% yield with high *trans* selectivity (15:1). Indole was also a good nucleophile and the corresponding product was isolated in 80-90% yield with lower *trans* selectivity (6:1).

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Scheme 1.

2. Synthesis of β -Mercapto Compounds

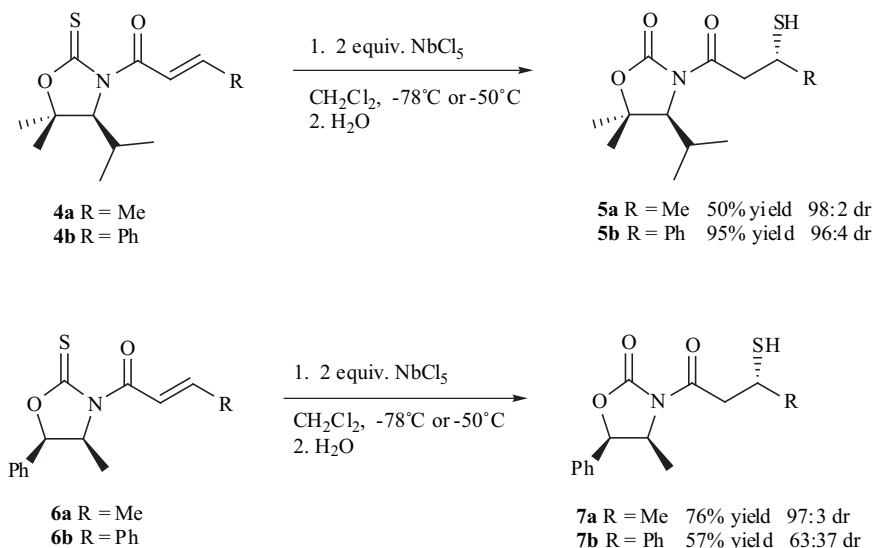
Ortiz and co-workers have demonstrated that niobium pentachloride is an efficient catalyst in the asymmetric sulfur addition reaction of *N*-enoyl oxazolidinethiones yielding β -mercapto products (Scheme 2) [8]. The *N*-enoyl oxazolidinethione **4** was prepared in several steps from *S*-valine and **6** directly from (1*R*,2*S*) norephedrine, followed by acylation with either crotonyl or cinnamoyl chloride.

The reactions were carried out in CH_2Cl_2 , at -78°C (-50°C for compounds **6**), and it was found that 2 equivalents of niobium pentachloride were necessary to promote the sulfur addition reaction of **4** and **6** giving the

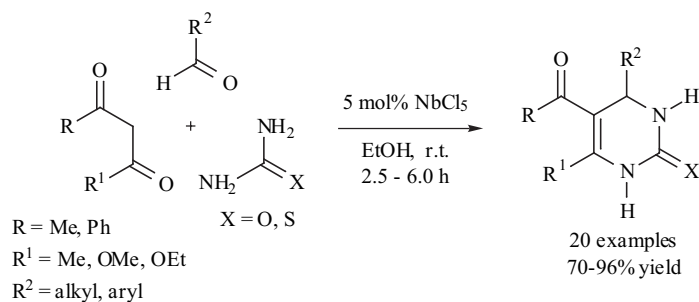
corresponding β -mercapto products **5** and **7**, respectively, in good yields and excellent diastereomeric ratios (except for **7b**). The *R* configuration of the stereogenic center on sulfur was established by X-ray analysis of compound **7a**.

Although the authors claim that the reactions proceed through an intramolecular sulfur transfer reaction, no detailed mechanistic study was presented to confirm this assumption.

Other Lewis acids were investigated such as SnCl_4 and TMSCl but these were not the choice to mediate this reaction because of low yields of products and long reaction times, respectively. The main advantages pointed out by the authors on the use of NbCl_5 in this reaction were the ease to



Scheme 2.



Scheme 3.

handling it and to follow the course of the reactions by change in the color, the high yields and stereoselectivities obtained and also no precipitate was formed in the reactions.

3. Synthesis of 3,4-Dihydropyrimidinones

3,4-Dihydropyrimidinones are found in the structure of several important alkaloids with a variety of interesting pharmacological properties [9]. Pyrimidinones are easily prepared from the three-component one-pot condensation of an aldehyde, 1,3-dicarbonyl compound and urea or thiourea under acidic conditions (Biginelli reaction) [10].

Yadav and co-workers reported the use of catalytic amounts of niobium pentachloride (5 mol%) as an efficient catalyst for the Biginelli reaction under extremely mild conditions [11]. The reactions were carried out in ethanol, at room temperature. Several substituted aldehydes and 1,3-dicarbonyl compounds were reacted with urea or thiourea to give the corresponding dihydropyrimidinones in excellent yields with high purity (Scheme 3).

Lower temperature, higher yields, shorter reaction times and the ability to tolerate a variety of functional groups were some of the advantages listed by the authors over other methods previously described in the literature.

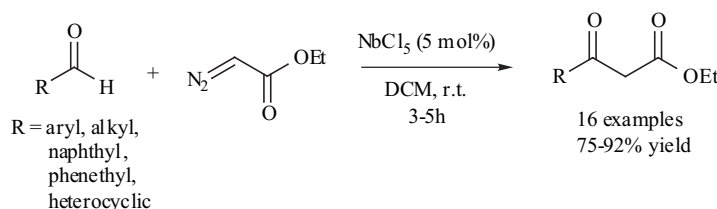
4. Synthesis of β -Keto Esters

β -Keto esters can be easily prepared by carbon-carbon bond formation through C-H insertion of diazoacetates into aldehydes under acidic conditions [12]. Yadav and co-workers have demonstrated that niobium pentachloride is an efficient catalyst in the synthesis of various β -keto esters using a similar protocol [13]. Several aromatic and aliphatic aldehydes were reacted with ethyl diazoacetate in the presence of 5 mol% of NbCl_5 affording the corresponding β -keto esters in excellent yields with high selectivity under mild conditions (Scheme 4). No side products or polymerization reactions were observed when substrates containing sensitive groups, such as furfural, were used.

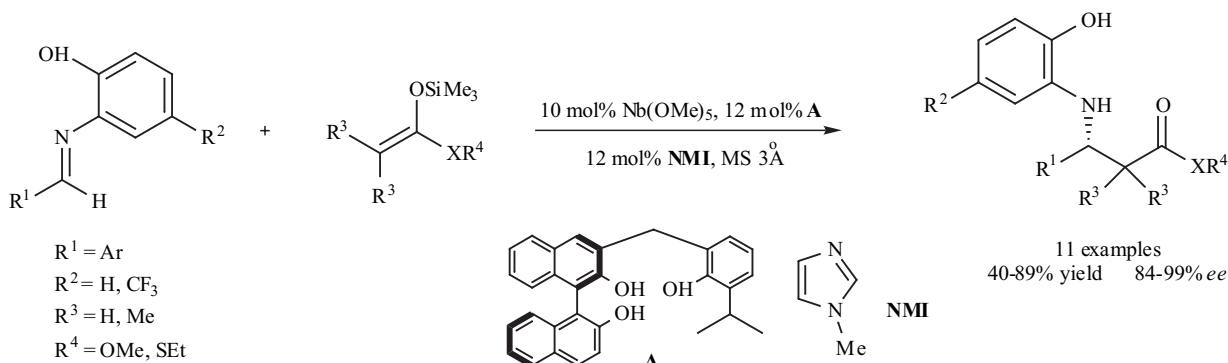
Other Lewis acids such as InCl_3 , $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, TaCl_5 and GdCl_3 were also used but NbCl_5 was found to be the best catalyst for this conversion. The major drawback of this methodology was that ketones and other diazoacetates did not furnish any condensation product.

5. Mannich-Type Reactions Using Chiral Niobium Complexes

Kobayashi and co-workers synthesized a new dinuclear chiral niobium complex from niobium alkoxides, *N*-methylimidazole (NMI) and different tridentate chiral ligands



Scheme 4.



Scheme 5.

[14]. These new chiral niobium complexes were prepared *in situ* and employed as catalysts in Mannich-type reactions.

It was observed that the enantioselectivities were better when the reactions were carried out in toluene-CH₂Cl₂ (1:1) mixed solvent system using MS 3Å or MS 4Å as additive. Catalytic amounts of the chiral niobium complex (2-10 mol%) efficiently promoted the addition of the silicon enolates to several imines affording the corresponding β -amino compounds in excellent yields and selectivities as shown in Scheme 5.

Experiments of nonlinear effect (NLE) [15] and ¹H- and ¹³C-NMR analysis revealed the possible structure of the highly selective niobium catalyst in solution (Fig. 1). Interestingly, the X-ray structure obtained was slightly different indicating a decomposition of the active species, probably, according to the authors, through the cleavage of the C-O bond of the bridging ethoxy group of **8**, followed by Nb-O-Nb bond formation.

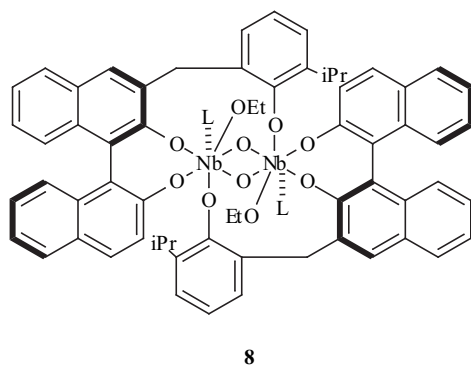
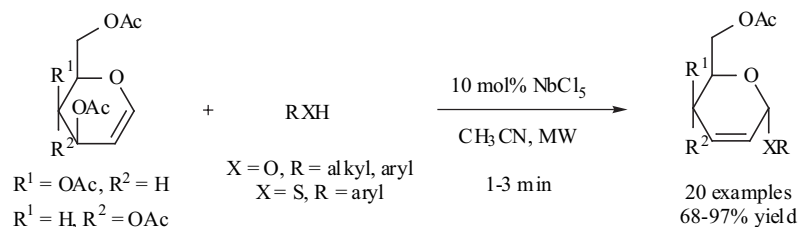


Fig. (1).

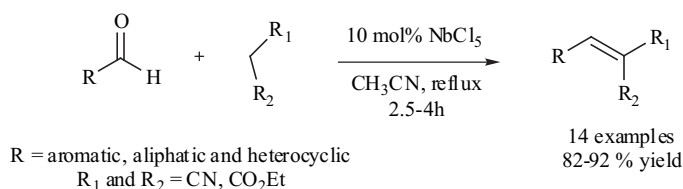
6. Ferrier Reaction [16]

Hotha and Tripathi have studied the use of catalytic amounts of NbCl₅ to promote the Ferrier reaction under microwave irradiation conditions to yield 2,3-unsaturated *o*-glycosides that are versatile intermediates in the synthesis of several natural products [17].

It was observed that as low as 1 mol% of NbCl₅ efficiently promoted the S_N2' attack of a variety of alcohols



Scheme 6.



Scheme 7.

and thiols to per-*O*-acetylated glycols. The reactions were carried out in acetonitrile under microwave irradiation furnishing the corresponding 2,3-unsaturated glycosides in good yields with α -stereoselectivity, in short reaction times, as shown in Scheme 6. Allylic, benzylic, aliphatic and monosaccharide alcohols were used as well as phenol and thiophenol.

Other methods using a variety of different Lewis acids and oxidizing agents have been described but some drawbacks were listed by the authors such as varying yields and selectivities, harsh reaction conditions and long reaction times as compared to the methodology using NbCl₅.

7. Knoevenagel Condensation

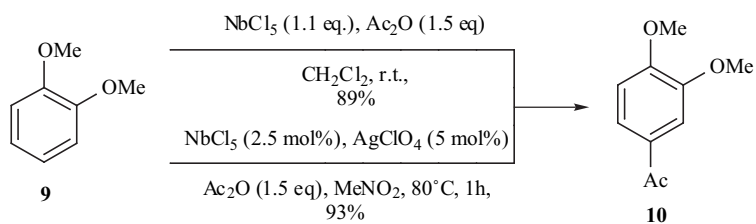
Leelavathi and Kumar demonstrated the efficiency of niobium pentachloride as Lewis acid to promote the Knoevenagel condensation between an aldehyde and an active methylene compound yielding electrophilic alkenes under mild conditions [18]. The reactions of several aldehydes and active methylene compounds were carried out in acetonitrile, under reflux conditions, to give the Knoevenagel products in excellent yields with high stereoselectivity (Scheme 7). In all cases, the *E*-olefin was obtained exclusively, demonstrating the high stereoselectivity of the process.

Catalytic amounts of NbCl₅ (10 mol%) were employed, this method being better when compared to other previously reported methods under heterogeneous conditions that require stoichiometric amounts or a large excess of the catalyst and harsh reaction conditions. Furthermore, they lack in generality.

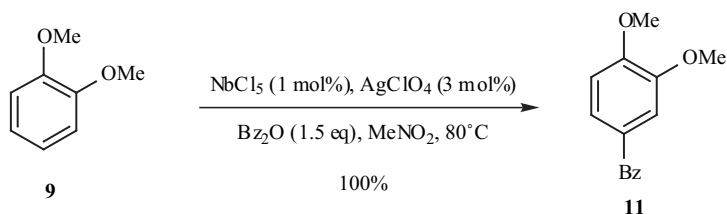
8. Friedel-Crafts Acylation

Recently, Nishida and co-workers have demonstrated the use of NbCl₅-AgClO₄ system as an efficient catalyst to promote the Friedel-Crafts acylation of several aromatic compounds [19].

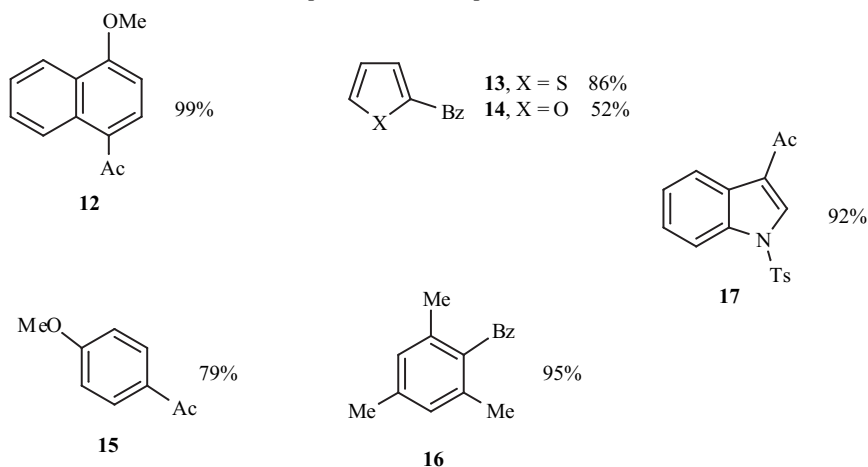
The Friedel-Crafts product **10** was obtained in 89% yield when a slight excess of NbCl₅ (1.1 equivalent) was used (Scheme 8). In contrast, when a catalytic amount of NbCl₅



Scheme 8.



Other representative examples

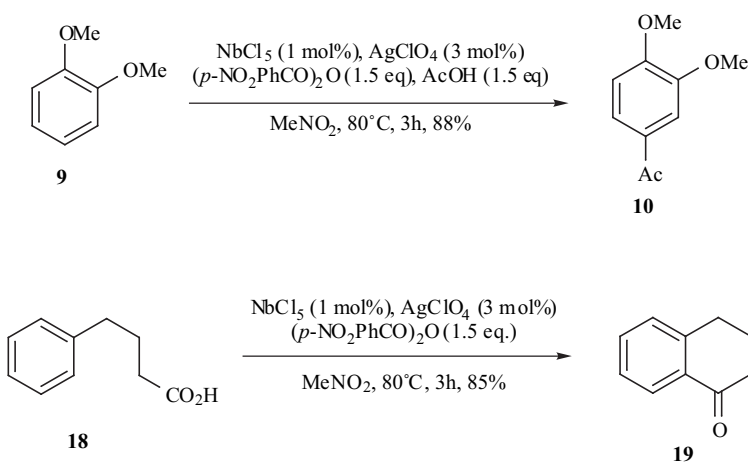


Scheme 9.

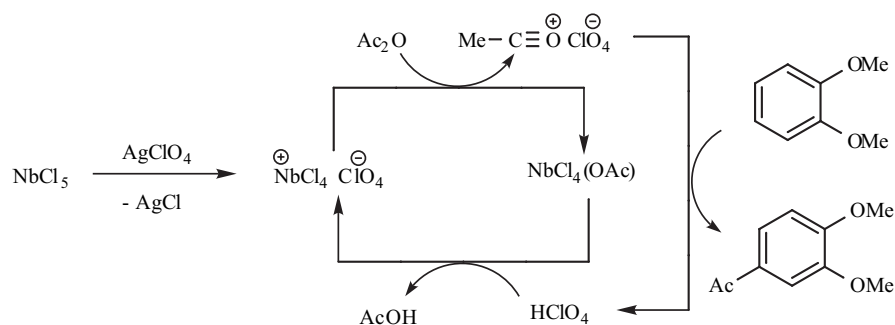
(10 mol%) was used the corresponding acylated product was formed in low yield (19%). However, in the presence of catalytic amounts of a co-catalyst (AgClO_4), it was also possible to employ catalytic amounts of NbCl_5 (2.5 mol%) and the corresponding acylated product was isolated in 93% yield. The best results were obtained when the reactions were carried out in nitromethane at 80°C . The experiments

showed that both catalysts were essential for the success of the reaction.

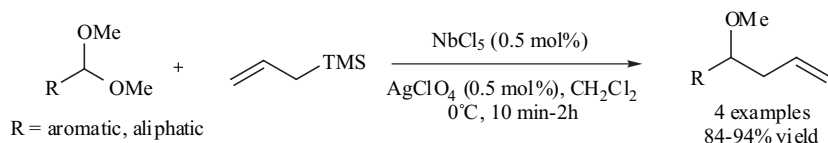
Acetic and benzoyl anhydrides were used as acylating agents with a variety of aromatic compounds to furnish the corresponding Friedel-Crafts products in good to excellent yields (Scheme 9).



Scheme 10.



Scheme 11.



Scheme 12.

Carboxylic acids in the presence of *p*-nitro-benzoic anhydride were also used as acylating agents and the corresponding Friedel-Crafts products were isolated in good yields (Scheme 10).

The authors proposed a catalytic cycle in which a new niobium complex is formed through the reaction of NbCl_5 and AgClO_4 , which reacts with acetic anhydride to give an oxonium salt. Subsequent nucleophilic addition of the aromatic compound and regeneration of aromaticity with loss of hydrogen furnish the corresponding acylated product (Scheme 11).

9. Allylation of Acetals

This same system (NbCl_5 - AgClO_4) was also successfully used to promote the addition of allyltrimethylsilanes to acetals [19]. In this protocol, 0.5 mol% of both catalysts was enough to give the Sakurai-Hosomi products in excellent yields (Scheme 12).

10. Tetrahydropyranylation of Alcohols and Phenols

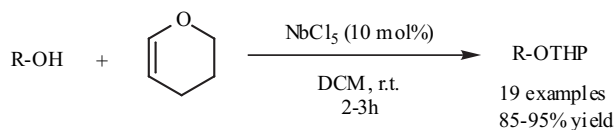
The protection and deprotection of functional groups are very important reactions in organic synthesis and several

methods are known [20]. Recently, Nagaiah and co-workers found that catalytic amounts of NbCl_5 (10 mol%) efficiently promoted the protection of alcohols and phenols using 3,4-dihydro-2H-pyran (DHP) as protecting group [21]. A variety of alcohols and phenols were treated with a slight excess of DHP in the presence of NbCl_5 in dichloromethane, at room temperature, affording the respective THP-ethers in excellent yields under mild conditions (Scheme 13). It was not observed any side reactions with sensitive groups present on substrates under acidic conditions.

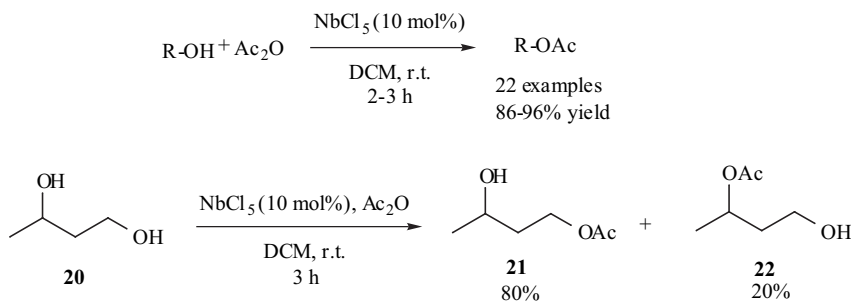
Shorter reaction times, better yields and greater tolerance of functional groups present on substrates are some advantages listed by the authors for this method using NbCl_5 over other methods already known.

11. Acetylation of Alcohols and Phenols

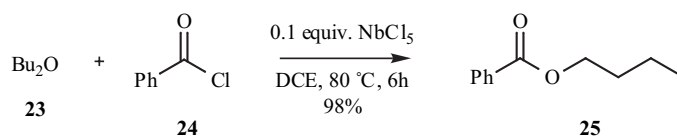
Catalytic amounts of NbCl_5 (10 mol%) were found to promote the selective acetylation of alcohols and phenols, at room temperature, under mild conditions [22]. Several alcohols were investigated and the corresponding acylated products were obtained in good yields with high regioselectivity to the less sterically hindered hydroxy



Scheme 13.



Scheme 14.



Scheme 15.

group, for example, when butane-1,3-diol **20** was used (Scheme 14).

A wide range of functional groups are tolerated and no side products were formed when substrates containing sensitive groups were used. A comparative reactivity study was performed and the authors proposed the following reactivity order: phenolic > benzylic > aliphatic primary > aliphatic secondary > aliphatic tertiary.

12. Acylative Cleavage of Ethers

Takahashi and co-workers reported the use of MoCl_5 as catalyst to promote the formation of esters using several ethers and acyl chlorides affording the corresponding esters in moderate to excellent yields (39-99%) [23].

Then, a comparative study using several metal halides from groups 5 and 6 (WCl_6 , NbCl_5 , TaCl_5) and other Lewis acids such as ZnCl_2 , TiCl_4 , AlCl_3 and SnCl_4 as catalysts for the acylative cleavage of dibutyl ether and benzoyl chloride was performed. The authors pointed out that a catalytic amount of NbCl_5 (10 mol%) was enough to promote the acylative cleavage of dibutyl ether and the corresponding butyl benzoate was isolated in 98% yield (Scheme 15).

The mechanism proposed by the authors is slightly different from the conventional mechanism that involves the generation of cationic species. Here, no oxonium ion is formed through the reaction between the Lewis acid and the acid chloride, instead a simultaneous attack of an alkoxyde to $\text{C}=\text{O}$ and subsequent attack of Cl^- to Cl_4MoOR re-

generates the catalyst (MoCl_5), giving the corresponding ester (Scheme 16). We believe this same mechanism could be applied to NbCl_5 as well.

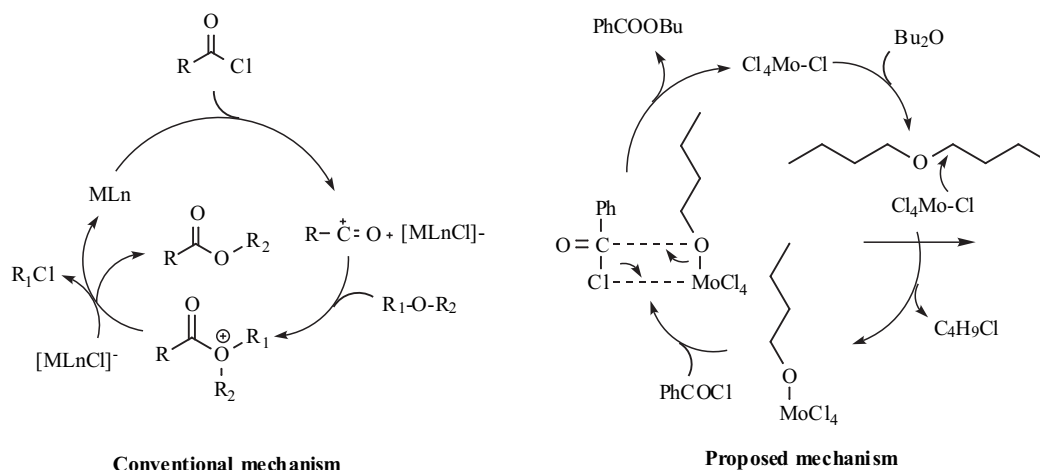
13. Synthesis of 1,3,5-triaryl-1,5-dihalo-1,4-pentadienes

Yadav and co-workers reported the use of GaCl_3 as catalyst to promote the synthesis of 1,3,5-triaryl-1,5-dihalo-1,4-pentadienes through the condensation between aldehydes and aryl acetylenes [24]. In most cases, the reactions afforded exclusively *E,Z*-isomers. In this study, the authors pointed out that catalytic amounts of NbCl_5 (20 mol%) were also successfully employed in this conversion but the yields were not reported (Scheme 17).

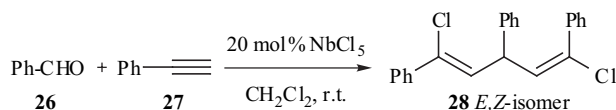
14. Diels-Alder

Júnior and co-workers reported the application of niobium pentachloride as Lewis acid in Diels-Alder reactions between cycloenones and cyclopentadiene [25]. Different cycloenones with an excess of cyclopentadiene (5 equivalents) were added to a solution of NbCl_5 (50 mol%) in diethyl ether and the corresponding Diels-Alder adducts were isolated in moderate to good yields with high conversion (100%) in most cases (Scheme 18). The reactions were investigated in three different temperatures (-78°C , r.t. and under reflux) and the best stereoselectivities were obtained at lower temperature.

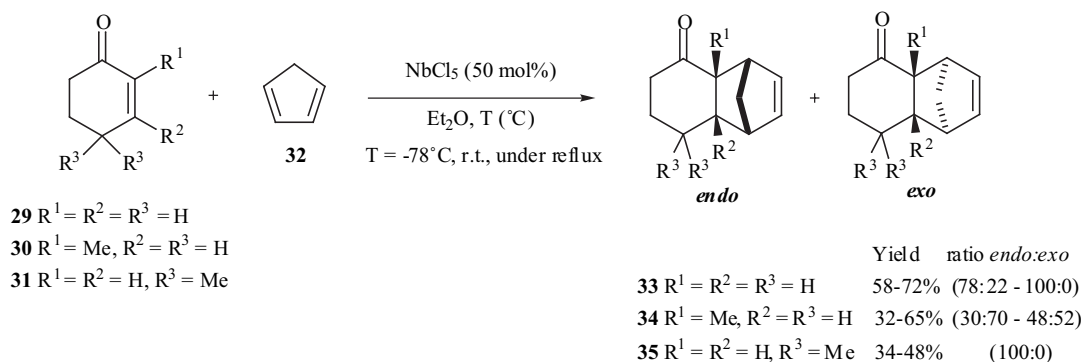
The best results were obtained when unsubstituted 2-cycloenones were used, while no product was observed when β -methyl substituted cycloenones were applied. Higher



Scheme 16.



Scheme 17.



Scheme 18.

stereoselectivities (100:0) favoring the *endo* isomer were observed when γ,γ -dimethyl substituted 2-cycloenone was used.

The authors pointed out some advantages such as shorter reaction times, lower temperatures and diene excess and higher stereoselectivity in most cases for this approach using NbCl_5 as catalyst over other methods described in the literature.

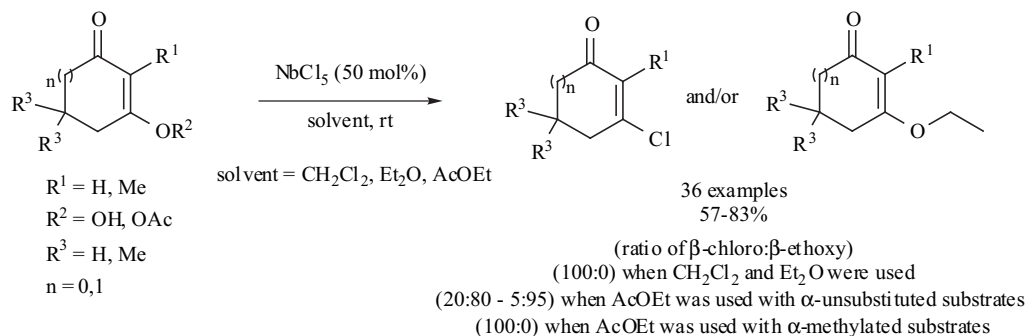
15. Synthesis of β -Chloro- α,β -Unsaturated Ketones

Constantino and co-workers demonstrated the use of NbCl_5 as an efficient catalyst for the synthesis of β -chloro- α,β -unsaturated ketones under mild conditions [26]. Several β -diketones were reacted with different amounts of NbCl_5

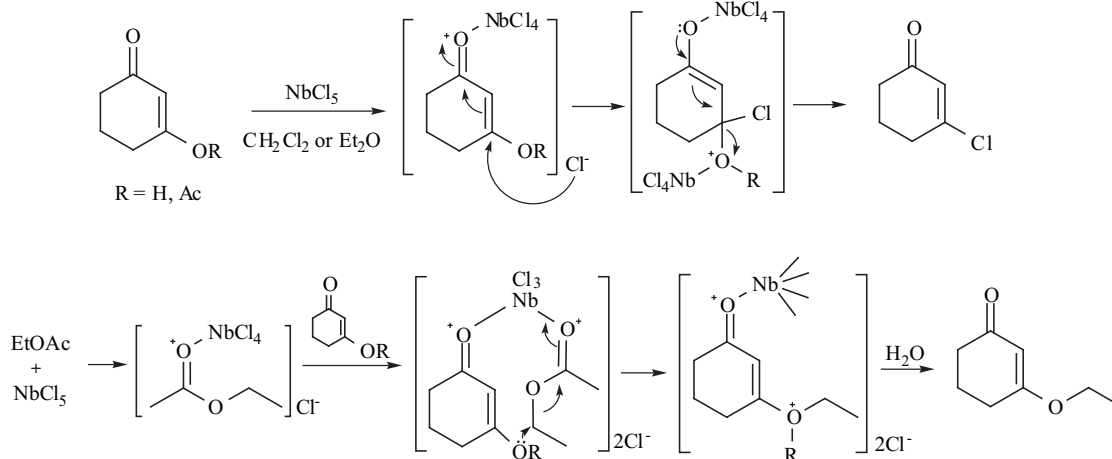
giving the corresponding β -chloro- α,β -unsaturated ketones in good yields (Scheme 19). In most cases, 50 mol% of NbCl_5 was necessary to promote the conversion.

For all substrates, an exclusive formation of β -chloro- α,β -unsaturated ketones was obtained when dichloromethane and ethyl ether were used. However, the formation of β -chloro compounds in ethyl acetate could only be accomplished when α -methylated enones were used. β -ethoxy enones were obtained as side products when the α -unsubstituted substrates reacted with NbCl_5 in AcOEt .

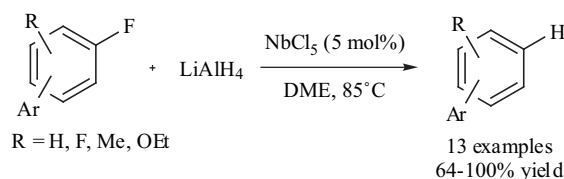
The mechanism proposed by the authors for the formation of β -chloro compounds involves the attack of chloride ion to the β -position of the enone complexed with NbCl_5 followed by elimination of NbCl_4OR , whereas the



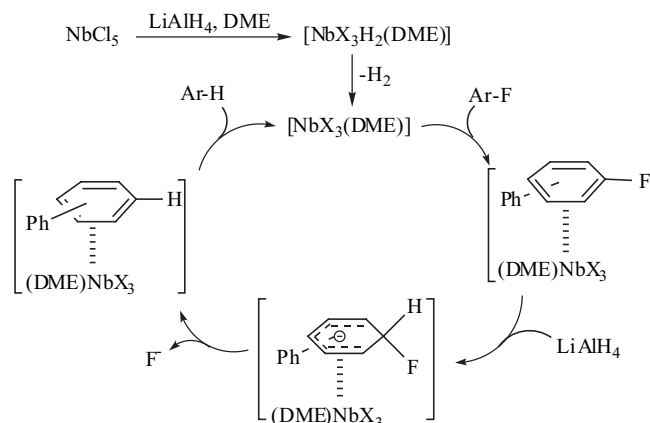
Scheme 19.



Scheme 20.



Scheme 21.



Scheme 22.

mechanism proposed for the formation of β -ethoxy compounds involves the attack of the substrates to ethyl acetate complexed with NbCl_5 (Scheme 20).

16. Low-Valence Niobium Compounds

The use of low-valence niobium as catalyst has been reported for a wide range of interesting coupling reactions [5]. Nb(III) can be easily prepared through a reduction reaction of NbCl_5 using LiAlH_4 , zinc powder or $^n\text{Bu}_3\text{SnH}$ as reducing agents. The following recent examples are representative.

16.1 - Dehalogenation of Fluoride Compounds

Fuehbe and Akiyama reported the dehalogenation of organic compounds using low-valence niobium generated through the reduction reaction between NbCl_5 and LiAlH_4 [27]. A comparative study using different metal halides of group 5 was examined and niobium pentachloride was the most effective catalyst for this conversion.

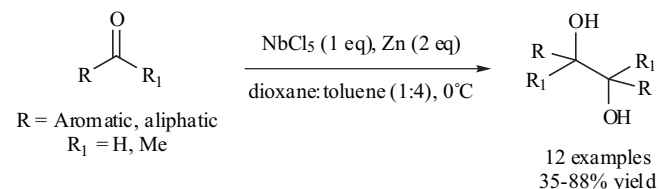
It was found that 5 mol% of NbCl_5 was enough to promote the dehalogenation reaction of several substrates in good yields. The reactions were carried out under reflux conditions and 1,4-dioxane was the best solvent employed (Scheme 21).

Among all substrates used, the authors observed that the *ortho*- and *para*-isomers are more reactive compared to the *meta*-isomer. The best results were obtained when biphenyl substrates were used. For instance, when the aromatic ring is substituted with a benzyl group instead of a phenyl group, the dehalogenated product was obtained in only 13% yield. The proposed mechanism involves the aromatic nucleophilic addition of LiAlH_4 to the complex formed through the interaction of Nb(III) and fluoroarene. Subsequent elimination of fluoride and regeneration of the catalyst furnish the corresponding dehalogenated compounds (Scheme 22).

16.2 - Pinacol Coupling

Arai and co-workers reported the use of low-valence niobium in the pinacol coupling of aldehydes and ketones furnishing the corresponding 1,2-diols [28]. The Nb(III) used was freshly generated *in situ* through the reduction reaction between NbCl_5 and zinc powder to subsequent coupling reaction.

It was necessary to use a stoichiometric amount of NbCl_5 (1 equivalent) and an excess of Zn powder (2 equivalents) to furnish the corresponding 1,2-diols from a variety of aldehydes and ketones in good yields and high diastereoselectivities (Scheme 23). The best results were obtained when 1,4-dioxane/toluene (1:4) solvent system was used. The authors pointed out that the generality of the substrates is still low especially when ketones are used.



Scheme 23.

CONCLUDING REMARKS

The works discussed in this review demonstrate the efficiency and versatility of niobium catalysts, especially NbCl_5 , when applied to organic synthesis. As already anticipated, our expectation is that their applicability will grow even more and many more interesting examples shall appear. In most cases, their advantages over other common Lewis acids are notable and the search for new methodologies involving niobium compounds will continue to attract the attention of research groups worldwide.

ACKNOWLEDGEMENTS

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