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A REVIEW ARTICLE ON "THE ROLE OF ORGANOMAGNESIUM IN THE SYNTHESIS OF PYRIDYL-THIAZOLE"

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ABSTRACT:
The present review attempts to bring out some important and significant developments of pyridyl-thiazole heterocyclic compounds in pharmaceutical sector, in the world of thiopeptide antibiotics, in the area of luminescence and pyridyl-thiazole as a Ligand in coordination chemistry in recent years. The general purpose of this article is to give an exhaustive and clear picture in biheteroaryl, thiazole-pyridyl bond formation as well as its application in the synthesis of natural products, pharmaceuticals, catalyst, ligands and materials. Accordingly, this review aims to systematize the current information in this field and provide some perspectives about some cross coupling reactions using Grignard Reagent.

Key Words: - Biheteroaryl, Fluorescent, polydentate ligand, Cytoprotective,

INTRODUCTION:-

In past few years, organic chemists are enormously taking efforts to reinforce unique, well organized and productive methods for the formation of heteroaryl-heteroaryl linkage with magnificent selectivity and high functional group liberality under lenient reaction conditions this is because of the crucial importance of the biheteroaryls & their homologues, tetraheteroaryls, oligoheteroaryls and polyheteroaryls in the organic chemistry.

In different branches of chemistry such as in medicinally vital drugs, polymers, various natural products, co-ordination complexes, etc the biheteroaryl compounds play an important role. Although the thiazole -pyridine is not the amongst the most studied biheteroaryl compound but it plays significant role in the pharmaceuticals. The biheteroaryls acts significantly as fungicide[1] or prohibitors for 5-lipogenase[2] these characteristics differs on the basis of type of groups attached to them. These scaffolds also play a very important role in the medicinal chemistry since the bihetereoaryl compounds like pyridyl thiazole are cytotoxic to human cells(including both cancerous & non-cancerous) but when they are coordinated with ruthenium(II) precursor $[Ru(\eta 6\text{-p-cymene})Cl_2]_2$ strongly increase the anticancer/cytoprotective activity[3].

These pyridyl thiazole complexes are acts as polydentate ligands (may be chelating). Among the polydentate ligands of this kind, nucleophilic, multifunctional thiazole, isothiazole and thiadiazole-based derivatives have an extraordinary importance in the construction of metal complexes of different types, particularly organometallic frameworks and functional

materials. Due to the favored structural arrangements in substituted 1,3thaizoles bonded with aryl and heteroaryl groups have a lot of applications in different subsidiaries such as in material science (Liquid Crystals)[2], (molecular switches)[4],they are also used in the production of cosmetics that have dermal protection properties (i.e. Sunscreens and lotions)[5].

The molecular fluorescent switches are one of the highly developing branch exceedingly they can be used as chemo-sensors for variety of species with biological significance. It was found that dyes are composed of a thiazole derivative skeleton which acts as photographic sensitizer.

The general intension of this review is to provide thorough and clear idea about the different coupling methods for the bond formation between biheteroaryl,pyridyl-thiazole using organomagnesium reagants (Grignard reagent). As a result, this appraisal aims to put in order the existing information in this field and provide a disciplined approach for cross coupling reactions using organomagnesium reagents this vital group of coordination compounds.

- ***Coupling reactions using organomagnesium reagents(Grignard's Reagent) :-***

a. Negishi Coupling reaction using Grignard's reagent:-

The heteroaryl nucleophiles may react with a suitable sulfur (IV) containing starting product which supplies us with a transitory sulfurane. Alkyl sulfinates were engaged to evade competing coupling reaction in first step. Later it was simplify that activation of the sulfinate oxygen, followed by cross coupling reactions with 2-pyridyl Grignard of its starting product gives analogue for pyridyl-thiazole as shown in (Scheme -a)[6]

b. Negishi Coupling Reaction using Organomagnesium Reagent

An additional heteroaryl nucleophile reacts with the sulfur moiety containing starting compound this supplies us a temporary sulfuran.Alkyl sulfinates were used to avoid rival coupling reaction in initial step. In final step it was generalized that the introduction of the sulfunate oxygen,follows cross coupling reactions with **3 equivalents of 2-thiazoly Grignard reagent** of the starting product gives 70% of Pyridyl thiazole as represented in (Scheme -b)[6]

c. Stille Coupling using Grignard reagent for synthesis of pyridyl thiazole derivative: - When the treatment of heteroaryl nucleophile with the sulfur moiety containing scaffold is done, provides us a provisional sulfuran. Alkyl sulfinates were employed to escape adversary coupling reaction in first step. In final step it was taken in a broad view that the insertion of the sulfunate oxygen, results a cross coupling reactions with **Grignard reagent titrated with I_2** of the starting product gives 81% of Pyridyl thiazole as shown in (Scheme-c)[7]

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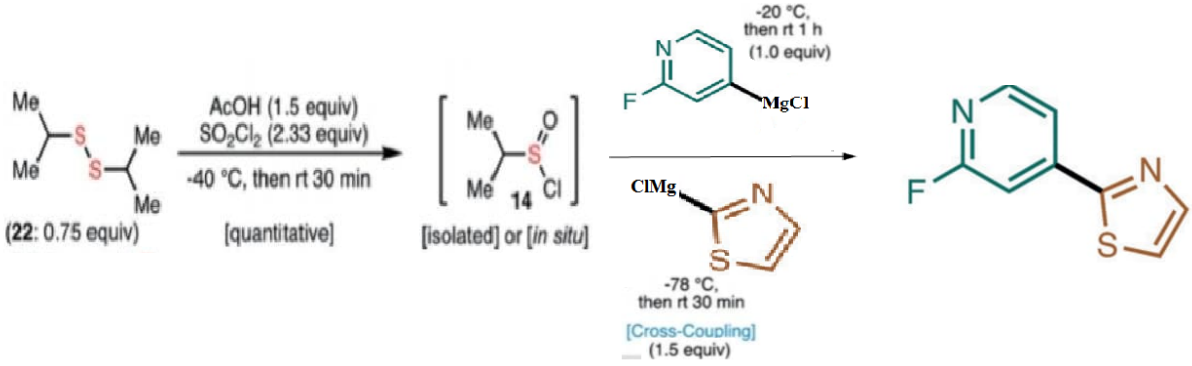
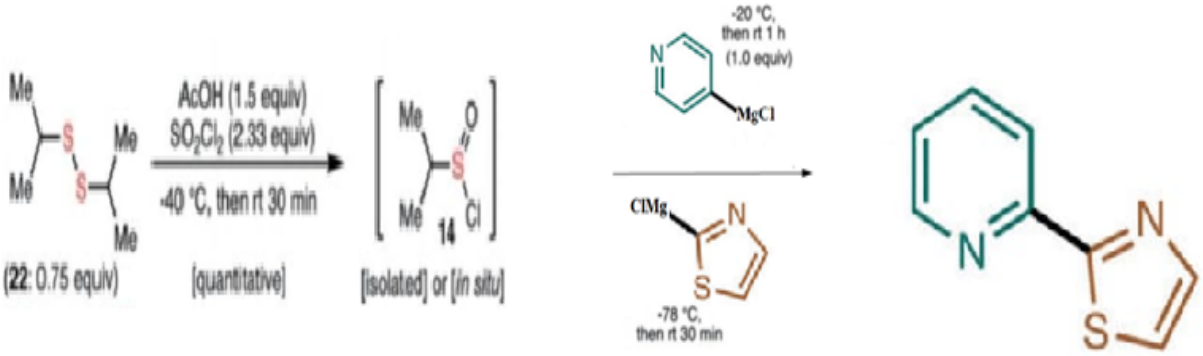
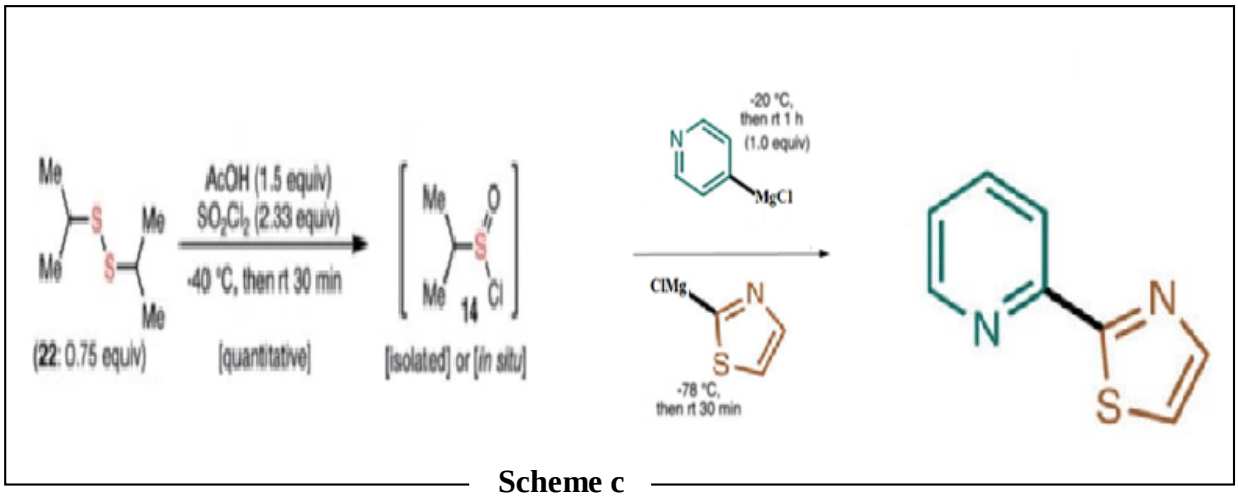


Scheme a



Scheme b


Me
Me
S
S
Me
Me
(22: 0.75 equiv)
AcOH (1.5 equiv)
SO_2Cl_2 (2.33 equiv)
-40 °C, then rt 30 min
[quantitative]
Me
O
S
Me
Cl
14
[isolated] or [in situ]
-20 °C,
then rt 1 h
(1.0 equiv)
N
MgCl
ClMg
N
S
-78 °C,
then rt 30 min
N
N
S

Scheme c