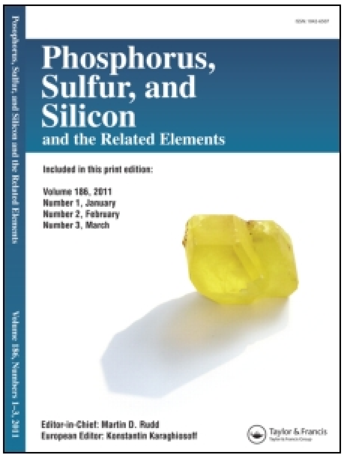

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Newer Aspects in Synthetic Methodology of Pyridyl Chalcogen (ESe/Te) Compounds

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Newer Aspects in Synthetic Methodology of Pyridyl Chalcogen (E=Se/Te) Compounds

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A number of synthetic protocols for the synthesis of symmetrical dipyridyl chalcogenides / dichalcogenides have successfully been developed by employing cheap, economically viable and eco-friendly reagents. The reductive cleavage of Se—Se and Te—Te bond in these versatile compounds conveniently have been achieved and a number of hitherto unknown chelating seleno / telluro ethers with varying back bones have been prepared employing appropriate alkylating agents.

Keywords Pyridine; selenium; tellurium

INTRODUCTION

Chemistry of alkyl aryl and mixed alkyl aryl chalcogenides R_2E and dichalcogenides R_2E_2 (E=Se/Te) is well documented[1,4] and lately has been the subject of renewed interest because of its diverse applications especially in electronics, opto-electronics and organic synthesis. It is curious to note that the corresponding chemistry of pyridyl derivatives of Se and tellurium has not merited special attention of practicing chemists. It probably is due to lack of convenient synthesis that the interesting aspects of the chemistry of these compounds have not been exploited. Commonly used methods for the preparation of pyridyl chalcogen compounds are time consuming, cumbersome, and involve either too-high or too-low temperatures. Recently, only pyridyl chalcogen compounds have emerged as important synthons in the organic chemistry[5,6] and have found varied applications in the field of biochemistry.[7,9] Due

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to the mismatch of hardness-softness of the nitrogen and the chalcogen in these compounds, they offer interesting coordination behavior.[9,11] The complexes of pyridyl chalcogenides with various transition metals have been shown to serve as single source precursor for MOCVD[12,13] studies. In view of these applications, we directed our efforts toward the convenient synthesis of these compounds.

RESULT AND DISCUSSION

Attempts to prepare 2-selenopyridines were first made by Mautner et al.[14] employing the reaction of hydrogen selenide with 2-bromopyridine at elevated temperatures in ethylene glycolmonoethylether. The most discouraging aspect of the methodology was the use of poisonous hydrogen selenide gas. Since then, developing a convenient and scalable methodology for the synthesis of these compounds has remained a subject of interest. In continuation of our work in this field,[15,16] efforts were aimed at synthesizing these compounds on molar scale using cheap and easily available reagents.

We focused our preliminary investigations on the use of sodium borohydride[17] as a reducing agent for the preparation of title compounds. Sodium borohydride reduces elemental selenium/tellurium to NaHE or Na_2E_2(where E=Se, Te) depending upon the molar ratio of the reagents used (Scheme 1).

$$E + NaBH_4 \xrightarrow[\text{2-ethoxyethanol} \atop \text{reflux}]{\text{ethanol /}} NaHE + B(OC_2H_4OC_2H_5)_3/B(OC_2H_5)_3 + 3\,H_2$$

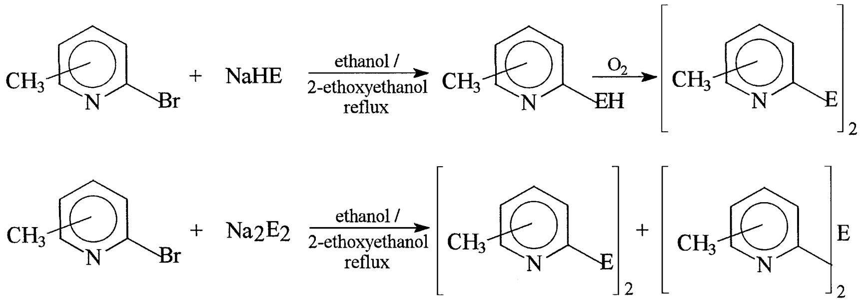
$$3E + NaBH_4 \xrightarrow[\text{2-ethoxyethanol} \atop \text{reflux}]{\text{ethanol /}} Na_2E_2 + B(OC_2H_4OC_2H_5)_3/2B(OC_2H_5)_3 + 6H_2$$

SCHEME 1

2-pyridyl seleno/telluro were prepared by the reaction of sodium hydrogen selenide/telluride with the corresponding 2-bromopyridine in refluxing ethanol or 2-ethoxyethanol (Scheme 2). These were then subjected to aerial oxidation for the preparation of 2,2′-dipyridyldichalcogenides.

The present methodology was extended to realize the selective synthesis of 5-bromo and 3,5-dibromo substituted 2,2′-dipyridyl diselenides/ditellurides.

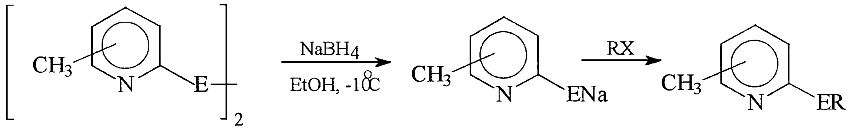
During the course of this investigation on the preparation of various substituted 2,2′-dipyridyldiselenides/ditellurides, the formation of corresponding monoselenides, and monotellurides respectively was invariably accompanied in minor yield as a by-product.



(E = Se, Te)

SCHEME 2

Sodium borohydride was also employed for the cleavage of Se—Se/ Te—Te bond of these diselenides/ditellurides (Scheme 3). This cleavage followed by alkylation yielded unsymmetrical pyidylselenium/tellurium compounds.



E = Se, Te

(R = $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$)

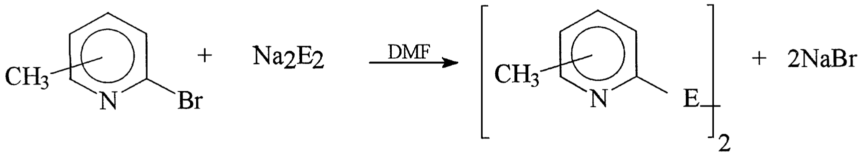
SCHEME 3

The above methodology offered good yields. An attempt to use more easily available reagent hydrazine hydrate as a reducing agent proved to be an attractive route (Scheme 4). In this methodology elemental selenium/tellurium was reduced to diselenide/ditelluride anion in alkaline medium. This diselenide/ditelluride anion thus formed react *in situ* with various bromopyridines to afford the title compounds in good to excellent yield

In addition the selenium-selenium bond in these dipyridyl diselenides reductively were cleaved using hydrazine hydrate in alkaline medium to give pyridylselenoate anion. This anion upon reaction with various halomethanes yields various 2-pyridylselenomethanes.[18]

Hydrazine hydrate was not able to reduce elemental tellurium to ditelluride anion efficiently unless the elemental tellurium is made active but successfully reduces the tellurium-tellurium bond of

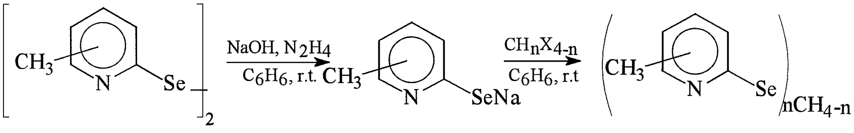
$$4\,E + N_2H_4 + 4\,NaOH \xrightarrow{DMF} 2\,Na_2E_2 + 4\,H_2O + N_2$$



E = Se, Te

SCHEME 4

2,2′-dipyridyl ditelluride. This reduction followed by alkylation give unsymmetrical 2,2′-pyridyl tellurium compounds (Scheme 5).[19]



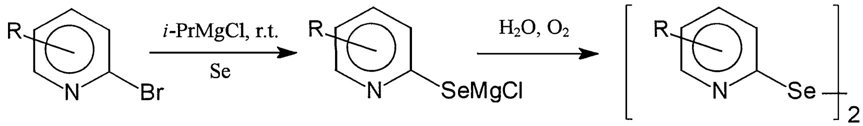
n = 1-3

SCHEME 5

The above methodology was also carried out in the presence of various phase transfer catalysts viz: polyethylene glycol-400, tetrabutylammonium bromide. The interfacial mechanism of the reaction for the preparation of the unsymmetrical pyridyl chalcogen compounds was proposed.

In order to study the utility of various organolithium and organomagnesium reagents toward the synthesis of title compounds we first tried the lithiation of pyridine using BF_3.[20] The deprotonation of BF_3 complexed pyridine was accomplished at 2-position with the use of highly hindered base lithium tetramethyl piperidine in ether at −78°C to give BF_3 complexed 2-lithiopyridine. This complex upon addition of elemental selenium/tellurium followed by oxidation gave 2,2′-dipyridyldiselenides/tellurides.

The above reaction was carried out under cryogenic conditions which are rather difficult to maintain for the synthesis on molar scale. In order to simplify the conditions we carried out the bromine-magnesium exchange of 2-bromopyridine using various Grignard reagents to afford pyridyl magnesium halides (Scheme 6). Meunier et al[21] carried out bromine-magnesium exchange of 2-bromopyridine with isopropylmagnesium chloride in THF to obtain pyridyl magnesium chloride, and later Queguiner et al[22] reported the trapping of this reagent with different electrophiles. No attempts have been made to study utility of



SCHEME 6

this exchange toward the synthesis of pyridyl selenium compounds. This pyridyl magnesium halide was quenched with elemental selenium/tellurium followed by the treatment with acidified water give corresponding dipyridyldiselenide/ditelluride in good to excellent yields. This exchange was found to be most efficient in case of isopropylmagnesium halide.

The above methodology was then extended toward the selective mono bromine-magnesium exchange[23] of 2,5-dibromopyridine and 2,3,5-tribromopyridines. Interestingly it was found that in case of 2,5-dibromopyridine the selective exchange took place at C-5 of the pyridine ring whereas in the case of 2,3,5-tribromopyridine it occurred at C-3 of the pyridine ring. Various symmetrical[24] as well as unsymmetrical[25] 2,2′dibromo-5,5′-dipyridyldiselenides/tellurides have been prepared and fully characterized by NMR, elemental analysis, and mass spectral studies.

In another approach, we tried the use of more hindered organometallic reagent n-Bu_3MgCl for the bromine-magnesium exchange. n-Bu_3MgCl was obtained by the reaction of n-BuLi(2 equiv) with n-BuMgCl(1 equiv) in toluene at −10°C. n-Bu_3MgCl was made to react with 2-bromopyridine to generate mono metalated intermediate. Addition of three equivalent of selenium to this intermediate followed by aerial oxidation give diselenides in good yields and ditellurides in moderate yields.[26]

Attempt to study the use of these 2-pyridyltellurides in organic synthesis by carrying out the tellurium-metal exchange of 2-alkyltelluropyridine with RMgX at room temperature was carried out. The exchanged product upon subsequent quenching with benzaldehyde in THF at room temperature gives phenyl(2-pyridyl)methanol in good yield.[26]

All the diselenides prepared were yellow solids, where as all the ditellurides were deep red in color except 3,3′-dimethyl-2,2′-dipyridylditelluride, which is deep blue in color. All the diselenides have a long shelf life where as all ditellurides are unstable in solution and decompose to give white solid of unknown composition. This may be the probable reason for low yields of the ditellurides as compared to diselenides.

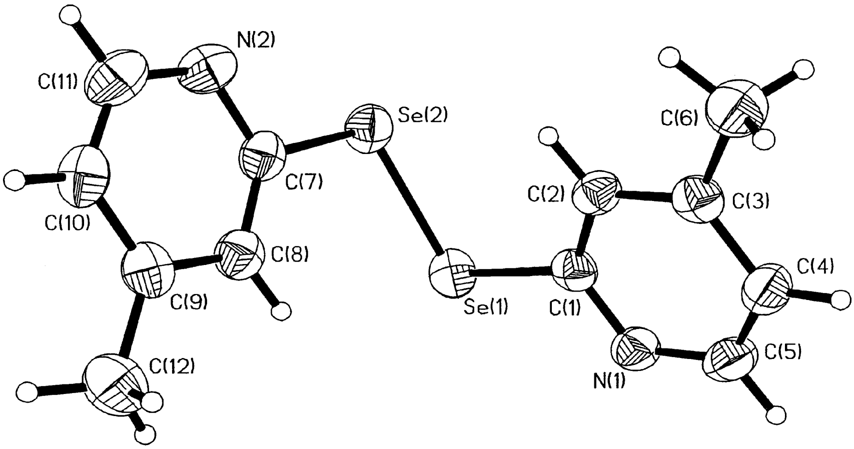


FIGURE 1 Crystal Structure of 4,4′-dimethyl 2,2′-dipyridyl diselenide with bond distances (Å) Se(1)—C(1): 1.938(4), Se(1)—Se(1)#1: 2.2973(7), and angles (°) C(1)—Se(1)—Se(2): 102.47(12), C(2)—C(1)—Se(1): 124.8(3).

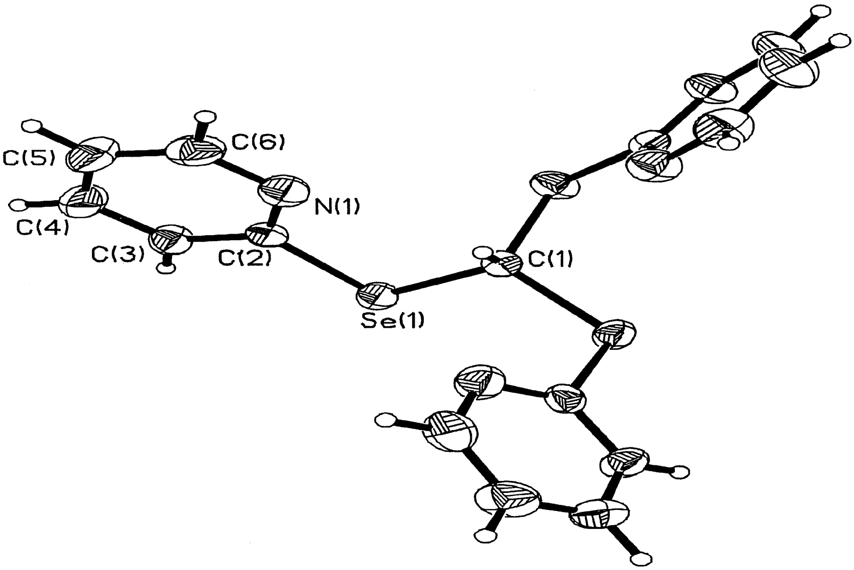


FIGURE 2 Crystal structure of tris(2-pyridylseleno)methane with bond distances (Å) Se(1)—C(1): 1.939(4), Se(1)—C(2): 1.918(6), and angles (°) C(2)—Se(1)—C(1): 100.3(3), C(3)—C(2)—Se(1): 115.9(4).

Solid State Structure Features

In order to understand the structural details, single crystals of several compounds have been grown and structures of 6,6′-; 4,4′-; and 3,3′-dimethyl-2,2′-dipyridyldiselenide and 5,5′-; 3,3′-dimethyl-2,2′-dipyridylditelluride, tris(2-pyridylseleno)methane, 2,2′-dipyridylditelluride, 6,6′-dimethyl-2,2′,5,5′-tetrabromo-3,3′-dipyridylditelluride, 2,2′,5,5′-tetrabromo-3,3′-dipyridylditelluride, 2,2′,5,5′-tetrabromo-3,3′-dipyridyldiselenide and 2-bromo-5-selenopyridyltribromomethane have been grown and analyzed by single crystal X-ray diffractometer. A perspective view of the representative structure of 4,4′dimethyl-2,2′-dipyridyldiselenide and tris(2-pyridylseleno)methane are given in Figures 1 and 2 with selected bond lengths and angles. Currently we are pursuing the coordinating aspects of these versatile pyridyl chalcogen compounds along with their application toward organic synthesis and material sciences.

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