International Journal of Chemical Science
Online ISSN: 2523-2843, Print ISSN: 2523-6075; Impact Factor: RJIF 5.22
Received: 20-10-2020; Accepted: 30-10-2020; Published: 14-11-2020
www.chemicaljournals.com
Volume 4; Issue 3; 2020; Page No. 38-45

Design, synthesis and characterisation of organochalcogenides from 2,3-Dibromopyridine

Dr. Shivani Gulati
Associate Professor, Department of Chemistry, DAV College, Chandigarh, India

Abstract

A novel method for the preparation of hitherto unknown symmetrical 2/3-bromo substituted pyridyl dichalcogenides (E = Se and Te) from 2,3-dibromopyridine is being reported. All the newly synthesized compounds have been characterized through elemental analysis employing various spectroscopic techniques, namely, NMR (^{1}H, ^{13}C, ^{77}Se, ^{125}Te), infrared and mass spectrometry.

Keywords: Organochalcogenides, 2,3-dibromopyridine, pyridyl dichalcogenides, spectroscopic techniques

Introduction

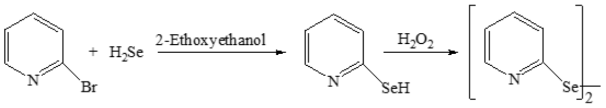
Organoselenium and organotellurium compounds are finding renewed interest as synthetic reagents in organic synthesis [1,2]. In addition to their synthetic applications, these compounds are fast gaining contemporary interest due to their indispensable applications in electronic industry [3], as organic conductors [4] and precursors for semiconducting materials [5], in biology [6] and in medical imaging.

It is curious to note that the chemistry of alkyl, aryl, and mixed alkyl aryl chalcogenides has developed rapidly for the last two decades and is of immense interest to organic chemists [7] and biochemists [8], whereas the chemistry of pyridyl derivatives virtually remained neglected, in spite of its greater utility [9]. Recently, the chemistry of pyridyl derivatives has attracted the attention of the scientific community due to their unique properties, which endear them to the new and exciting applications in organic synthesis. In recognition of its importance, renewed efforts have evolved for the convenient methodologies of their synthesis.

The presence of nitrogen in the aromatic ring brings remarkable changes and has attracted considerable attention of the practicing chemists as precursors in pharmacological compounds [10], for the preparation of liquid crystals [11], in the synthesis of polymers, and as ligands in transition metal complexes.

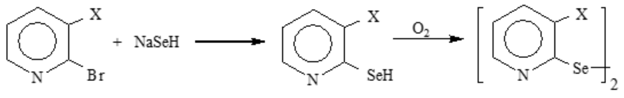
Results and Discussion

Initial efforts in pyridyl selenium chemistry were initiated by Mautner [12] *et.al.,* who prepared *Bis*(2-pyridyl) diselenide by the oxidation of 2-selenopyridine with hydrogen peroxide.



Toshimitsu[13] *et.al.,* and Smith[14] *et.al.,* reported a modified procedure for the synthesis of *Bis*(2-pyridyl) diselenide and *Bis*(3-hydroxy-2-pyridyl) diselenide which avoids the use of toxic hydrogen selenide gas.

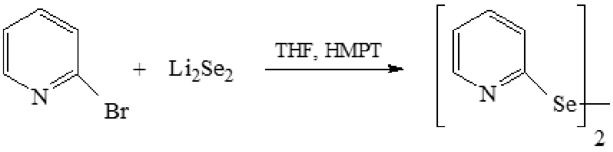
$$2\,Se + 2\,NaBH_4 \xrightarrow[\text{2-Ethoxy ethanol}]{\text{Ethanol /}} 2\,NaSeH + B(OC_2H_4OC_2H_5)_3/\,B(OC_2H_5)_3 + 3\,H_2$$



(X = H, OH)

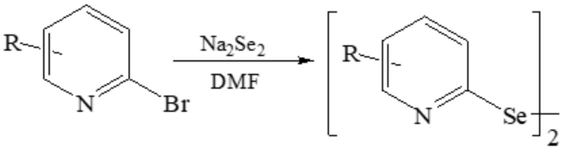
Syper and Mlöchowski[15] developed another methodology for *Bis*(2-pyridyl) diselenide by reacting dilithium diselenide with 2-bromopyridine.

$$2\,Se + 2\,Li \xrightarrow[20^{o}C]{THF} Li_2Se_2$$



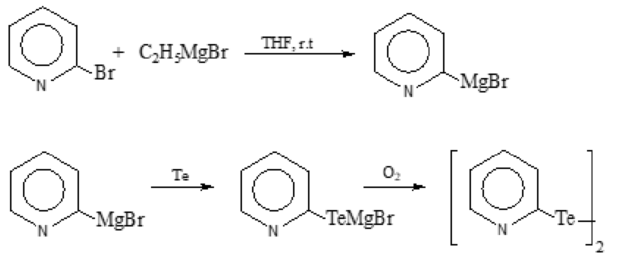
Bhasin[16] *et.al.,* have prepared various methyl substituted dipyridyl diselenides/ditellurides by the reaction of sodium hydrogen selenide/telluride using sodium borohydride with various methyl substituted 2-bromopyridine. Methyl substituted 2-pyridyl diselenides/ditellurides can also be prepared by using a mild and easily available reagent hydrazine hydrate.[17]

$$4\,Se + N_2H_4 + 4\,NaOH \longrightarrow 2\,Na_2Se_2 + H_2O + N_2$$



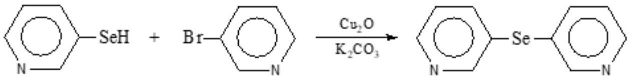
R = H, CH_3

Recently, an efficient one pot synthesis of symmetrical pyridyl monoselenides by the reaction of bromo-/iodopyridine with *i*-PrMgCl followed by quenching with selenyl chloride has been developed. Colonna[18] *et.al.,* synthesized *Bis*(2-pyridyl) ditelluride in low yield by insertion of elemental tellurium to pyridyl magnesium bromide, followed by aerial oxidation.

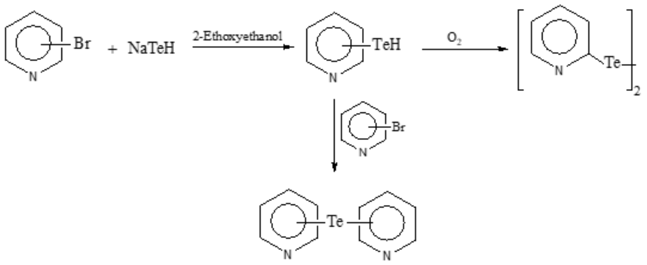


Tanji[19] *et.al.,* employed the reaction of 2-bromopyridine with lithium alkyl tellurolates while Kondu[20] *et.al.,* employed the nucleophilic substitution of 2-halopyridine with lithium 1-butyltellurolate anion to prepare alkyl pyridyl tellurides. Curiously, 3-pyridyl chalcogen compounds have not figured out predominately in the literature. Introduction of selenium/tellurium into the 3-position of a pyridine ring is rather difficult and a relatively few methods available for this purpose afford usually low yield[21] and are difficult to handle. In view of the tedious method adopted by Dunne[22] *et.al.,* for the synthesis of *Bis*(3-pyridyl) diselenide, a viable method for the preparation of *Bis*(3-pyridyl) diselenide/ditellurides is highly desirable.

Bis(3-pyridyl) diselenide has been prepared by reacting 3-pyridyl diazonium sulphate with potassium selenocyanate followed by oxidation with hypophosphorus acid in air.[24] Symmetrical *Bis*(2-pyridyl) selenide has been obtained by heating 3-bromopyridine and 3-pyridylselenol to 180 ºC in a sealed tube.

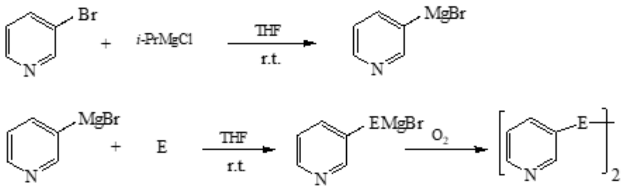


Liu[23] *et.al.,* prepared *Bis*(2-pyridyl) ditelluride by the reaction of 2-bromo pyridine with sodium hydrogen telluride in DMF followed by aerial oxidation. Dunne[22] *et.al.,* carried out the preparation of various dipyridyl ditellurides and tellurides by employing the reduction of elemental tellurium with sodium borohydride to sodium hydrogen telluride and its subsequent reaction with bromopyridines in 2-ethoxyethanol.



Magnesiated pyridines have been used as viable route for the functionalization of pyridines[24]. These can be prepared by magnesium-halogen exchange of bromopyridines using Grignard reagents. It is noteworthy that the lithiated pyridines are known to decompose at room temperature while the magnesiated pyridines are stable at room temperature for many hours. In addition, the more covalent character of C-Mg bond compared to C-Li bond tolerates the presence of various functional groups on the pyridine ring.

An efficient one-pot synthesis of *Bis*(3-pyridyl) diselenides/ditellurides has been developed by trapping magnesiated pyridines with the elemental selenium/tellurium[25].



E = Se, Te

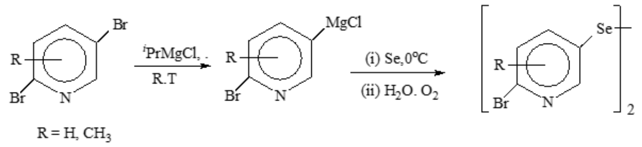
Dibromopyridines are versatile heterocyclic compounds. Their unique reactivity has been nicely exploited in syntheses of ligands[26] and bioactive molecules. Depending on the position of bromines on the pyridine ring selective functionalizations can be realized. In this context, halogen-lithium exchange has received much attention and efficient methodologies have been developed to control the exchange regioselectivity. The nature of the solvent, the lithiating agent and the temperature were found to have dramatic effects on the reaction outcome. Isomerization of 2-lithiopyridine into the thermodynamically favoured 5-lithiopyridine can be prevented by using toluene as non-coordinating medium. Although, directed metallation or selective bromine/lithium-exchange provides a convenient protocol to prepare a range of lithiated heterocycles, the high polarity of the carbon-lithium bond precludes the presence of sensitive functional groups in these lithium organometallics due to their too high reactivity.

Halogen-magnesium exchange reactions are preferred for generating pyridylmagnesium halides since the direct access to pyridine Grignard reagents by the oxidative addition of magnesium to the halopyridine is difficult to achieve, even with magnesium activation. A survey of literature reveals that iodine-magnesium exchange can be observed when the iodides were treated with alkyl or phenylmagnesium halides. Paradies[27] observed chlorine-magnesium exchange in a reaction of chloropyridines with phenylmagnesium halides. In case of bromopyridines, Paradies carried out bromine-magnesium exchange using phenylmagnesium halides while Meunier[28] used isopropylmagnesium chloride. The resulting Grignard derivatives were trapped with electrophiles.

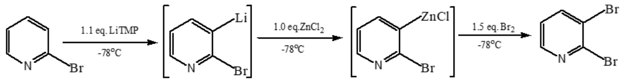
Quèguiner has successfully reported a regioselective Br/Mg-exchange in various isomeric dibromopyridines. [29] 2,6-Dibromopyridine undergoes a facile single Br/Mg-exchange with *i*-PrMgCl and give the monobrominated Grignard reagent in nearly quantitative yield. The synthesis of these polyfunctional Grignard reagents is, however, a problem, since the insertion of magnesium metal to aryl or heteroaryl halides bearing electron-withdrawing groups is inhibited by the presence of these functionalities. Recently, it has been shown that the halogen/magnesium-exchange reaction offers unique method for the preparation of a range of new functionalized heteroaryl magnesium compounds for synthetic purposes. These functionalized organomagnesium compounds have an excellent reactivity towards a wide range of electrophiles and readily undergo transmetallation to provide a wide variety of organometallic reagents and display an excellent chemoselectivity.

Chemo-selectivity has been also observed for 2,5-dibromopyridine affording only 2-bromo-5-magnesiated pyridine via single chemoselective Br/Mg-exchange under similar conditions. Subsequent treatment with iodine gives 2- bromo-5-iodopyridine in excellent yield. A single Br/Mg-exchange has also been found in case of the symmetrical 3,5-dibromopyridine affording 3-bromo-5-substituted pyridine.

A single bromine-magnesium exchange in case of 2, 5-dibromopyridine and 2-bromo-5-iodopyridine with *i*-PrMgCl was accomplished successfully at C-5 in THF at room temperature followed by addition of elemental selenium/tellurium. Aerial oxidation gives *Bis*(2-bromo-5-pyridyl)diselenide/ditelluride[30] in respectable yields.

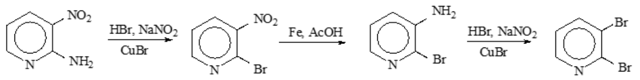


Before discussing the regioselectivity of bromine-magnesium exchange in case of 2,3-dibromopyridines, the preparative method for 2,3-dibromopyridines deserves a special mention. 2,3-dibromopyridines can be prepared by the lithiation of 2-bromopyridines using lithium teramethylpiperidine at -78°C to give 2-bromo-3-lithiopyridine. Transmetalation of the aryllithium intermediate with zinc chloride give an arylzinc species which upon bromination result in the formation of 2,3-dibromopyridines. [31]



Scheme 1: Methodology for the synthesis of 2,3-dibromopyridine

2,3-dibromopyridine can also prepared conveniently by the diazotization of 3-nitro-2-aminopyridine[32] followed by the reduction with iron in the presence of acetic acid and subsequent diazotization as shown.

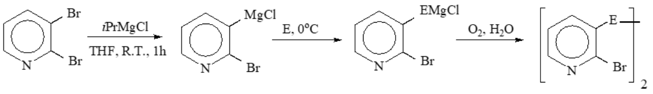


2,5-dibromopyridine compared to 2,3-dibromopyridine is a readily available material. Consequently there have been a number of reports on the regioselective cross coupling of this compound. A number of regioselective couplings[33] like Stille coupling, [34] Suzuki coupling [35] and even Kumada[36] type coupling have surfaced in the literature.

It is curious to note that there is no reference in the literature for the preparation of organochalcogen derivatives from starting from 2,3-dibromopyridines. It was, therefore, thought worth to explore the chemistry of these 2,3-dibromopyridine derivatives of selenium and tellurium especially the corresponding diselenides/ditellurides. As part of the ongoing studies on the synthesis of dipyridyl dichalcogenides *via* bromine-magnesium exchange, the subject has been elaborated towards 2, 3-dibromopyridines with an aim to study regioselective synthesis of bromo-substituted pyridyl chalcogen compounds.

Given the general electronic similarities of the 3- and 5-positions of pyridine, it was thought that the same set of reaction conditions may be directly translated to the substitution of bromine in case of 2,3-dibromopyridine.

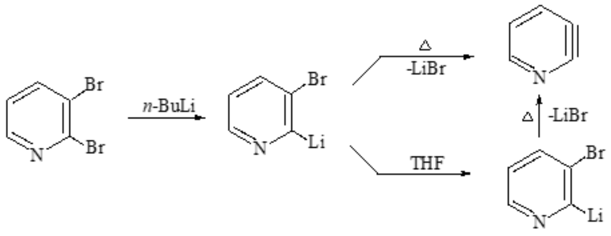
It was found that 2,3-dibromopyridine reacted smoothly with isopropyl magnesium chloride at room temperature to give red colored solution. The intermediate, 2-bromo-3-pyridylmagnesium chloride was trapped with elemental selenium or activated tellurium to give the corresponding, 2-bromo-3-pyridylseleno/telluromagnesium chloride, which upon subsequent oxidation gave *Bis*(2- bromo-3-pyridyl) diselenide and ditelluride in good yield (Scheme 2).



Scheme 2: Reaction scheme for the synthesis of *Bis*(2-bromo-3-pyridyl) diselenide and ditelluride

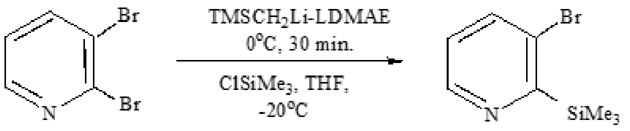
THF used as a solvent in the reaction is a non-coordinating solvent and can be easily removed on a rota evaporator. The observed selectivity of the exchange could be related to the strength of the carbon-bromine bond. Conjugation of the bromine at C-2 with C=N bond could justify the regioselective reaction at C-3.

The methodology discussed above has unique advantages over lithiation as it does not require cryogenic condition. Lithiation often requires low temperatures which are not easy to realize. In addition, bromine-lithium exchange has to be usually performed at low temperature (-100 °C in THF or around -40 °C in diethyl ether) in order to avoid of side reactions such as deprotonation, addition to the substrate, elimination of lithium bromide[37] (to give pyridynes), bromine migration[38] ("dance") or even ring opening reaction[39]. The presence of vicinal bromines in 2,3-dibromopyridine is a drawback for the selectivity of lithiation reactions. The potential isomerization of lithiated species results in the formation of pyridyne upon elimination of lithium bromide. It could also occur when the reaction is performed under non-cryogenic conditions[40].



Isomerization and degradation during lithiation of 2, 3-dibromopyridine

C-2 lithiation in case of 2, 3-dibromopyridine using TMSCH$_2$Li–LDMAE in hexane-toluene has recently been discovered by Gros and Elaachbouni[41]. The reaction was achieved under non-cryogenic conditions without formation of pyridyne and isomerization. This clean process has opened access to a range of 2-functional 3-bromopyridine synthons



Selective exchange product at C-3 position is obtained because the metal-halogen exchange takes place efficiently at C-3 position of the pyridine ring giving 2-bromo-3-pyridylmagnesium chloride rather than 3-bromo-2-pyridylmagnesium chloride. This is because, in the later case, inter electronic repulsions due to co-planarity of lone pair on the nitrogen of the pyridine ring with electrons of carbon-magnesium bond at C-2 position destabilizes the 2-magnesiated pyridine.

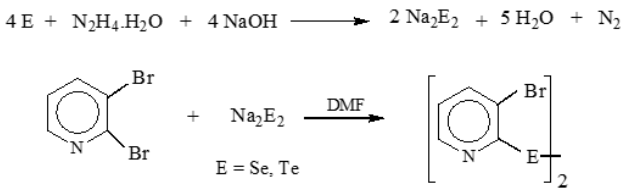
It is important to point out here that the use of equimolar amount of 2,3-dibromopyridine and *i*-PrMgCl resulted in poor yield. However, a slight excess of *i*-PrMgCl increases the yield considerably. The conditions throughout the reaction were maintained extremely dry, as even traces of moisture can hinder the insertion of elemental chalcogen into the pyridylmagnesium halide generated *in situ*. The efficiency of the reaction was also compared using different Grignard reagents *viz.,* ethyl magnesium bromide and *n*-butyl magnesium chloride. The results show that sterically hindered Grignard reagent results in the better yield.

In a representative method, 2,3-dibromopyridine (20.0 mmol) was added drop wise to a vigorously stirred solution of *i*-PrMgCl (20.0 mmol) in tetrahydrofuran. After 2h of continuous stirring at room temperature, elemental selenium/tellurium (20.0 mmol) was added at 0ºC. When all the selenium/tellurium had dissolved, the reaction was quenched with acidified water. The mixture was extracted with diethyl ether (4 x 100 ml) and the organic layer was dried over anhydrous sodium sulphate. Diethyl ether was removed and the residue thus obtained was purified by column chromatography using silica gel and hexane-ethylacetate (5:1) as eluant to yield pure diselenide/ditelluride.

The present reaction is completed in a couple of hours, making it one of fastest methodologies used for the synthesis of the organochalcogen compounds. After successful substitution of bromine at C-3 position by chalcogen to prepare *Bis*(2-bromo-3-pyridyl) diselenides/ ditellurides, it was decided to substitute bromine at C-2 position in 2,3-dibromopyridine to prepare *Bis*(3-bromo-2-pyridyl) diselenides/ditellurides. Therefore, it was thought of exploiting the versatility of a convenient, readily available and inexpensive reducing agent *i.e.,* hydrazine hydrate towards the synthesis of these compounds. The potential of hydrazine hydrate has already been established in our laboratory on 2,5-dibromopyridine[11] and the present study in continuation constitute an important aspect on the chemistry of 2,3-dibromopyridine.

During the course of these investigations, it was found that the addition of 1.0 equivalent hydrazine hydrate to 2.0 equivalent of elemental selenium suspended in DMF containing sodium hydroxide under nitrogen atmosphere resulted in the instantaneous evolution of nitrogen and simultaneous formation of dark green homogeneous solution of diselenide, Se_2^{2-} anion. The resulting solution was attempted to react with 2,3-dibromopyridine that resulted in the formation of *Bis*(3-bromo-2-pyridyl)diselenide in good yields.

The scheme of the reaction is as follows:



Scheme 3: Methodology for the synthesis of *Bis*(3-bromo-2-pyridyl)diselenide/ ditelluride

This methodology was further extended to synthesize the ditelluride anion by reduction of elemental tellurium in DMF with hydrazine hydrate in the presence of sodium hydroxide. The anticipated product obtained by reacting disodium ditelluride with 2,3-dibromopyridine was *Bis*(3-bromo-2-pyridyl) ditelluride thereby leading to conclusion that diselenide/ditelluride anion preferably attacks position C-2 of the 2,3-dibromopyridine. The formation of *Bis*(3-bromo-2-pyridyl) diselenide/ditelluride indicates that the inductive effect of nitrogen atom of pyridine makes the second position of pyridine ring more electophilic in comparison to C-3 position.

Experimental

All the manipulations were carried under a dry and deoxygenated nitrogen atmosphere to prevent the oxidation of oxygen-sensitive intermediates. Elemental sulphur, selenium, and tellurium (Sigma-Aldrich, Bangalore, India) were stored in a desiccator prior to use. Tetrahydrofuran (THF) was dried using sodium and benzophenone prior to use. Diisopropylamine (DIA) was distilled using CaH_2 and was stored on molecular sieves. 2-bromopyridines, *n*-butyl lithium of analytical grade were purchased from Aldrich and used without further purifi- cation. ^{1}H, ^{13}C, ^{77}Se and ^{125}Te NMR spectra were recorded on a Jeol AL spectrometer operating at 300, 75.432, 57.203, and 94.790 MHz, respectively in $CDCl_3$, using Me_4Si as an internal standard for ^{1}H and ^{13}C NMR. Me_2Se and Me_2Te were used as an external reference for ^{77} Se and ^{125}Te NMR. IR spectra were obtained between KBr plates on a Perkin-Elmer model 1430. C, H, and N analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Mass spectra were obtained on a VG-70S11-250J mass spectrometer. Separation and purifications of compounds were carried out using column chromatography performed on activated silica gel using hexane/ethyl acetate as eluant.

Synthesis of 2,3-dibromopyridine

To *n*-butyllithium in hexane (19.5 mL, 30.2 mmol) at -20ºC was added a solution of 2,2,6,6-tetramethylpiperidine (5.1 mL, 30.2 mmol) in THF (47.5 mL). After aging for thirty minutes, the solution was cooled to -78ºC and a solution of 2-bromopyridine (5.0 g, 3.0 mL, 27.0 mmol) in THF (28.0 ml) was added drop wise so as to maintain the temperature below -70 °C. After 2 h, a 1.0 M solution of $ZnCl_2$ in THF (27.5 ml, 27.5 mmol) was added drop wise and allowed to stir for an additional 30 min. Bromine (2.1 ml, 41.2 mmol) was added slowly at a rate to keep the temperature below -50 °C. The reaction was monitored by TLC. The reaction mixture was allowed to warm to 25 °C and finally quenched with water. The product was extracted with dichloromethane and the combined organic layers were washed in THF (28.0 mL) was added dropwise so as to maintain the temperature below -70ºC. After 2h, a 1.0 M solution of $ZnCl_2$ in THF (27.5 with 1 M HCl followed by washing with distilled water. The organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography with hexane to afford 6.0 g of 2, 3-dibromopyridine.

Synthesis of *Bis*(2-bromo-3-pyridyl) diselenide/ditelluride and *Bis*(3-bromo-2-pyridyl) diselenide/ditelluride

2,3-dibromopyridine (20.0 mmol) was added drop wise to a vigorously stirred solution of *i*-PrMgCl (22.0 mmol) in tetrahydrofuran (THF). After 2 h of continuous stirring at room temperature, elemental selenium/tellurium (20.0 mmol) was added to the reaction mixture in an ice bath. When all the selenium/tellurium had dissolved, the reaction was quenched with acidified water. The mixture was extracted with dichloromethane (4 x 100 ml) and the organic layer was dried over anhydrous sodium sulphate. Dichloromethane was removed and the residue thus obtained was purified by column chromatography using silica gel with hexane/ ethyl acetate as eluant to yield the pure diselenide/ditelluride.

Spectroscopic Studies

All the newly synthesized bromo substituted dipyridyl dichalcogenides are crystalline solids and are readily soluble in conventional organic solvents. The synthesized compounds have been characterized unambiguously with the help of elemental analysis and various spectroscopic techniques *viz.,* IR, ^{1}H NMR, ^{13}C NMR, $^{77}Se/^{125}Te$ NMR and mass spectral studies. The physical and analytical data of the newly prepared dichalcogenides are summarized in Table 1.

Table 1: Physical properties and elemental analyses of *Bis*(2-bromo-3-pyridyl)diselenide/ ditelluride and *Bis*(3-bromo-2-pyridyl)diselenide/ ditelluride

S. No.	Compound	M.p. (°C)	Yield (%)	Analytical Data % found (req. %)		
				C	H	N
1	2, 3-Dibromopyridine $C_5H_3NBr_2$	60.5	75	26.21 (25.35)	1.25 (1.28)	5.75 (5.91)
2	*Bis*(2-bromo-3-pyridyl) diselenide $(2\text{-}Br.C_5H_3NSe)_2$	152-153	50	25.15 (25.45)	1.33 (1.28)	5.75 (5.93)
3	*Bis*(2-bromo-3-pyridyl) ditelluride $(2\text{-}Br.C_5H_3NTe)_2$	180	45	21.21 (21.17)	1.02 (1.06)	4.86 (4.93)
4	*Bis*(3-bromo-2-pyridyl) diselenide $(2\text{-}Br.C_5H_3NSe)_2$	120-121	65	26.10 (25.45)	1.40 (1.28)	6.05 (5.93)
5	*Bis*(3-bromo-2-pyridyl) ditelluride $(2\text{-}Br.C_5H_3NTe)_2$	134-135	60	21.35 (21.17)	1.17 (1.06)	5.17 (4.93)

1H NMR Studies

^{1}H NMR spectra of *Bis*(2-bromo-3-pyridyl)diselenide/ ditelluride and *Bis*(3-bromo-2-pyridyl)diselenide/ ditelluride were obtained in $CDCl_3$ using TMS as an internal reference. ^{1}H NMR of bromo substituted diselenides and ditellurides show three signals corresponding to three pyridyl ring protons which appear in the range 7.18-8.54 (δ, *ppm*) and 7.05-8.40 (δ, *ppm*) in diselenides and ditellurides respectively.

As a representative example, ^{1}H NMR spectrum of *Bis*(2-bromo-3-pyridyl) diselenide exhibits one doublet at 8.14-8.15 (δ, *ppm*) for H-6 due to its coupling with meta protons of the ring, another doublet at 7.88-7.90 (δ, *ppm*) for H-4 and a multiplet for H-5 at 7.35-7.37 (δ, *ppm*). The detailed ^{1}H NMR spectra of the diselenides and ditellurides prepared during the course of the present studies are given in the Table 5.3.

^{13}C NMR studies

Carbon has two stable isotopes ^{12}C and ^{13}C found in 98.9 % and 1.1 % natural abundance. ^{12}C is magnetically inactive whereas ^{13}C is magnetically active. Magnetic moment of ^{13}C is one fourth to that of proton. Consequently, ^{13}C is less sensitive nucleus for NMR studies than proton. ^{13}C NMR chemical shifts are dependent on electron density and thus are useful for structural investigation of organometallic compounds. There have been numerous publications on the ^{13}C NMR studies of organometallic compounds.

Table 2: ^{1}H NMR spectroscopic data of *Bis*(2-bromo-3-pyridyl)diselenide/ ditelluride and *Bis*(3-bromo-2-pyridyl)diselenide/ ditelluride

S.No.	Compound	^{1}H NMR (δ, ppm)		
		H-6	H-4	H-5
1	2, 3-Dibromopyridine	8.14-8.15 (*d*, 1H, 1.8 Hz)	7.88-7.90 (*d*, 1H, 4.8 Hz)	7.35-7.37 (*m*, 1H)
2	*Bis*(2-bromo-3-pyridyl) diselenide	8.16-8.18 (*dd*, 2H, 4.8, 1.8 Hz)	7.79-782 (*dd*, 2H, 7.8,1.8 Hz)	7.14-7.22 (*m,* 2H)
3	*Bis*(2-bromo-3-pyridyl) ditelluride	7.93-8.05 (H-6, H-4) (*m*, 4H)	-	7.05-7.11 (*m*, 2H)
4	*Bis*(3-bromo-2-pyridyl) diselenide	8.53-8.54 (*d*, 2H, 1.8 Hz)	7.52-7.54 (*d*, 2H, 5.4 Hz)	7.41-7.44 (*m,* 2H)
5	*Bis*(3-bromo-2-pyridyl) ditelluride	8.38-8.40 (*d*, 2H, 1.8 Hz)	7.42-7.43 (*d*, 2H, 7.8 Hz)	7.32-7.34 (*m,* 2H)

^{13}C NMR of these compounds shows a set of five signals corresponding to the five magnetically non-equivalent carbons in the pyridyl ring. Compared to the aromatic hydrocarbons, heterocyclic ring carbon shielding covers a much broader range *i.e.* 100-170 *ppm*. Carbon bonded to the nitrogen atom is appreciably deshielded relative to the carbons of the benzene ring. Large variations are observed for the chemical shift value of the ring carbon directly attached to the selenium/tellurium. Detailed ^{13}C NMR chemical shifts of *Bis*(2-bromo-3-pyridyl) diselenide/ ditelluride and *Bis*(3-bromo-2-pyridyl) diselenide/ ditelluride are presented in Table 3.

Table 3: ^{13}C NMR spectral data of *Bis*(2-bromo-3 pyridyl)diselenide/ ditelluride and *Bis*(3-bromo-2-pyridyl)diselenide/ ditelluride

S.No.	Compound	C-2	C-3	C-4	C-5	C-6
1	2, 3-Dibromopyridine	141.8	123.4	135.7	125.1	146.9
2	*Bis*(2-bromo-3-pyridyl) diselenide	148.1	124.3	138.8	126.5	148.9

3	*Bis*(2-bromo-3-pyridyl) ditelluride	148.2	124.3	138.2	129.8	150.0
4	*Bis*(3-bromo-2-pyridyl) diselenide	150.3	118.5	140.2	125.5	151.9
5	*Bis*(3-bromo-2-pyridyl) ditelluride	142.0	119.4	138.1	132.2	150.8

^{77}Se NMR studies

^{77}Se NMR is an ideal tool for solving problems related to identification of structural and stereoisomers in selenium containing compounds. To obtain a correlation between the ^{77}Se atom chemical shift values of hitherto unknown bromo substituted pyridyl selenium compounds, the representative compounds were analyzed by ^{77}Se NMR. ^{77}Se NMR spectra of the bromo substituted diselenides were obtained in $CDCl_3$ with dimethyl selenide as an external reference. The values obtained have been tabulated in Table 4. ^{77}Se signal in *Bis*(2-bromo-3-pyridyl) diselenide (δ, 407.2 *ppm*) is observed upfield in comparison to *Bis*(3-bromo-2-pyridyl) diselenide (δ, 510.3 *ppm*).

^{125}Te NMR studies

Like ^{77}Se NMR, ^{125}Te has also proved to be a useful technique to investigate the metabolism and fate of the tellurium compounds in the biological systems. ^{125}Te NMR spectra of the bromo substituted dipyridyl ditellurides were obtained in $CDCl_3$ with dimethyl telluride as an external reference. The values are compiled in Table 4.

Table 4: ^{77}Se/^{125}Te NMR data of of *Bis*(2-bromo-3-pyridyl) diselenide/ ditelluride and *Bis*(3-bromo-2-pyridyl) diselenide/ ditelluride

S.No.	**Compound**	**^{77}Se/^{125}Te (δ, ppm)**
1	*Bis*(2-bromo-3-pyridyl) diselenide	407.2
2	*Bis*(2-bromo-3-pyridyl) ditelluride	431.5
3	*Bis*(3-bromo-2-pyridyl) diselenide	510.3
4	*Bis*(3-bromo-2-pyridyl) ditelluride	498.0

Mass spectral analysis

The isotopic richness of natural selenium and tellurium helps in the identification of selenium and tellurium containing fragments in the mass spectra of organoselenium and organotellurium compounds. A number of characteristic ions found in the mass spectra have been tabulated in Table 5.

Table 5: Mass spectral data of *Bis*(2-bromo-3-pyridyl)diselenide/ ditelluride and *Bis*(3-bromo-2-pyridyl)diselenide/ ditelluride

S.No.	**Compound**	***m/e***	**Relative Intensity**	**Assignment**
1	Bis(2-bromo-3-pyridyl) diselenide	474	52.5	$[C_{10}H_6N_2Br_2{}^{80}Se_2]^{+\cdot}$
		394	14.2	$[C_{10}H_6N_2Br_2{}^{80}Se]^{+\cdot}$
		314	57.4	$[C_{10}H_6N_2Se_2]^{+}$
		237	41.8	$[C_5H_3NBr^{80}Se]^{+\cdot}$
		234	3.0	$[C_{10}H_6N_2Se]^{+}$
		157	100	$[C_5H_3NSe]^{+}$
		154	50.0	$[C_{10}H_6N_2]^{+}$
		77	5.2	$[C_5H_2N]^{+}$
2	*Bis*(2-bromo-3-pyridyl) ditelluride	574	37.2	$[C_{10}H_6N_2Br_2{}^{130}Te_2]^{+\cdot}$
		444	35.5	$[C_{10}H_6N_2Br_2{}^{130}Te]^{+}$
		414	38.4	$[C_{10}H_6N_2{}^{130}Te_2]^{+\cdot}$
		287	62.3	$[C_5H_3NBr^{130}Te]^{+\cdot}$
		284	4.5	$[C_{10}H_6N_2Br]^{+}$
		157	6.5	$[C_{10}H_6N_2]^{+}$
		77	28.4	$[C_5H_3N]^{+}$
3	*Bis*(3-bromo-2-pyridyl) diselenide	474	85.5	$[C_{10}H_6N_2Br_2{}^{80}Se_2]^{+\cdot}$
		314	54.9	$[C_{10}H_6N_2Br_2]^{+}$
		237	15.5	$[C_{10}H_6N_2Se_2]^{+\cdot}$
		234	0.5	$[C_5H_3NBr^{80}Se]^{+}$
		157	100	$[C_5H_3NBr]^{+}$
4	*Bis*(3-bromo-2-pyridyl) ditelluride	574	14.5	$[C_{10}H_6N_2Br_2{}^{130}Te_2]^{+\cdot}$
		314	5.0	$[C_{10}H_6N_2Br_2]^{+\cdot}$
		287	0.8	$[C_5H_3NBr^{130}Te]^{+\cdot}$
		234	45.0	$[C_{10}H_6N_2Br]^{+}$
		154	12.5	$[C_{10}H_6N_2]^{+}$

IR Studies

This technique has been used for the general characterization of the newly prepared pyridyl selenium and tellurium compounds. IR spectra of these compounds were recorded in the range 4000-400 cm^{-1} in compressed transparent pellets made from powdered compounds and dry KBr. IR spectra of various compounds synthesized have been summarized in Table 6.

Table 6: Infrared spectral data of *Bis*(2-bromo-3-pyridyl)diselenide/ ditelluride and *Bis*(3-bromo-2-pyridyl)diselenide/ ditelluride

S.No.	**Compound**	**Important IR bands (KBr, cm^{-1})**
1	*Bis*(2-bromo-3-pyridyl) diselenide	3071, 2932, 1679, 1560, 1420, 1376, 1169, 1064, 668, 627, 550, 425
2	*Bis*(2-bromo-3-pyridyl) ditelluride	3041, 2990, 2959, 1635, 1528, 1485, 1398, 1124, 986, 925, 634, 510, 475
3	*Bis*(3-bromo-2-pyridyl) diselenide	3075, 2945, 1690, 1634, 1535, 1467, 1323, 1298, 1147, 1015, 576, 523, 429
4	*Bis*(3-bromo-2-pyridyl) ditelluride	3042, 2980, 1600, 1543, 1456, 1402, 1391, 1132, 975, 642, 575, 426

Acknowledgement

The author is thankful to University Grants Commission (UGC) for Teacher Fellowship and to Ph.D. mentors KK Bhasin and SK Mehta at Panjab University Chandigarh for introducing this frontier area of Organochalcogen Chemistry.

References

1. Wirth T, Ed. Organoselenium Chemistry, Modern Development in Organic Synthesis. Springer, New York, NY, USA, 2000.
2. Irgolic KJ. Organotellurium Compounds Houben-Weyl, Methods of Organic Chemistry. George Thieme, Stuttgart, Germany, 1990.
3. Singh HB, Sudha N. Organotellurium precursors for metal organic chemical vapour deposition (MOCVD) of mercury cadmium telluride (MCT). Polyhedron,1996:15:745-763.
4. Siato G, Kagoshima S, Eds. The Physics and Chemistry of Organic Superconductors. Springer, Berlin, Germany, 1990.
5. Somasundaram S, Chenthamarakshan CR, De Tacconi NR, Ming Y, Rajeshwar K. Photoassisted deposition of chalcogenide semiconductors on the titanium dioxide surface: mechanistic and other aspects. Chemistry of Materials,2004:16:3846-3852.
6. Hatfield DL, Ed. Selenium: Its Molecular Biology and Role in Human Health. Kluwer Academic, Boston, Mass, USA, 2001.
7. Patai S, Rappoport Z, Eds. The Chemistry of Organic Selenium and Tellurium Compounds, John Wiley & Sons, New York, NY, USA, 1986, 1.
8. Mugesh G, Du Mont WW, Sies H. Chemistry of biologically important synthetic organoselenium compounds. Chemical Reviews,2001:101:2125-2180.
9. Toshimitsu A, Hayashi G, Terao K, Uemura S. The pyridylseleno group in organic synthesis-part 5. Amidoseleniation of alkenes. Journal of the Chemical Society, Perkin Transactions1, 1988, 2113-2117.
10. Windscheif P-M, Vögtle F. Substituted dipyridylethenes and -ethynes and key pyridine building blocks. Synthesis, 1994, 87-92.
11. Seto K, Shimojitosyo H, Imazaki H, Matsubara H, Takahashi S. Synthesis of a new family of chiral smectic liquid crystals bearing a pyridine heterocycles. Chemistry Letters,1990:19:323-326.
12. Mautner HG, Chu SH, Lee CM. Studies of 2-selenopyridine and related compounds. Journal of Organic Chemistry,1962:27:3671-3673.
13. Toshimitsu A, Owada H, Uemura S, Okano M. An improved method for olefin synthesis using pyridylseleno group as a leaving group. Tetrahedron Letters,1980:21:5037-5038.
14. Smith K, Matthews I, Hulme NM, Martin GE. Novel heterocyclic systems. Part 21. Synthesis of 3-hydroxypyridine-2(1H)-selone and its application in the synthesis of 1-azaphenoxaselenine and its substituted derivatives. J. Chem. Soc. Perkin Trans.1, 1986, 2075-2079.
15. Syper L, Mlöchowski J. Lithium diselenide in aprotic medium - a convenient reagent for synthesis of organic diselenides. Tetrahedron,1988:44:6119-6130.
16. Bhasin KK, Jain VK, Kumar H, Sharma S, Mehta SK, Singh J. Preparation and characterization of methyl substituted 2,2′-dipyridyl diselenides, 2,2′-dipyridyl ditellurides, and their derivatives. Synthetic Communications,2003:33:977-988.
17. Bhasin KK, Singh J. A novel and convenient synthesis towards 2-pyridylselenium compounds: X-ray crystal structure of 4,4′-dimethyl-2,2′-dipyridyl diselenide and tris(2-pyridylseleno)methane. Journal of Organometallic Chemistry,2002:658:71.
18. Colonna FP, Distefano G, Galasso V, Irgolic KJ, Pappalardo GC, Pope L. Dipole moment and helium(I) photoelectron spectroscopic studies of the conformation of di-2-pyridyl and diphenyl dichalcogenides R2X2(X = S, Se, or Te). Journal Chemical Society Perkin Transaction,1981:2:281-285.
19. Sugimoto O, Sudo M, Tanji KI. Lithiation of 1H-pyrazolo[3,4-d]pyrimidine derivative using lithium alkanetellurolate. Tetrahedron Letters,1999:40:2139-2140.
20. Kondo Y, Shilai M, Uchiyama M, Sakamoto T. Preparation and reactions of 2-pyridyltellurium derivatives. Journal of Chemical Society Perkin Transaction 1, 1996, 1781-1782.
21. Bennet RD, Burger A, Volk WA. Communications - 3-Pyridylphosphonic Acid. Journal Organic Chemistry,1958:28:940.
22. Dunne SJ, Summers LA, Felsobuki EIVN. Synthesis of telluroBispyridines. Journal Heterocyclic Chemistry,1993:30:409-412.
23. Liu J, Qui M, Zhou X. Direct synthesis of some oiaryl ditellurides from aryl halides. Synthetic Communication,1990:20:2759-2767.
24. Bhasin KK, Arora V. Regioselective Synthesis of symmetrical pyridyl Selenium compounds by Bromine-Magnesium exchange of Bromopyridines using Isopropyl Magnesium Chloride: X-Ray Crystal structure of 2,2’,5,5’-Tetrabromo-3,3’-dipyridyldiselenide. Applied Organometallic Chemistry,2004:18:359-362.
25. Kumar R. Synthesis, characterisation and evaluation of some Sulphur, -Selenium and -Tellurium Compounds. Ph.D thesis, Panjab University Chandigarh, 2010.
26. Romero-Salguero FJ, Lehn JM. Synthesis of multitopic bidentate ligands based on alternating pyridine and pyridazine rings. Tetrahedron Letters,1999:40:859-862.
27. Paradies HH, Gorbing M. Angew. Chem. Int. Ed., A New Method for the Preparation of Organomagnesium Compounds of pyridine,1969:81:293.
28. Martin J, Mechin B, Paulmier C, Meunier JC. Etude par RMN des organomagnesiens heterocycliques de la serie du furanne, du thiofene, du selenofene et de la pyridine. Journal Organometallic Chemistry,1974:67:327-339.
29. Trecourt F, Gervais B, Mongin F, Marsais F, Quéguiner G. New syntheses of substituted pyridines via Bromine-Magnesium exchange. Tetrahedron,2000:56:1349-1360.
30. Bhasin KK, Arora V, Klapötke TM, Crawford MJ. One-Pot Synthesis of Pyridyltellurium Derivatives from a reaction with Isopropylmagnesium chloride and X-ray crystal structures of various pyridyl ditellurides. Europeon Journal of Inorganic Chemistry, 2004, 4781-4788.
31. Menzel K, Fisher EL, DiMichele L, Frantz DE, Nelson TD, Kress MH. An improved method for the bromination of metalated haloarenes via Lithium, Zinc

transmetalation: A Convenient Synthesis of 1,2-Dibromoarenes. Journal of Organic Chemistry,2006:71:2188-2191.

32. Bouillon A, Lancelot JC, Collot V, Bovy PR, Rault S. Synthesis of novel halopyridinylboronic acids and esters. Part 2: 2,4, or 5-Halopyridin-3-yl-boronic acids and esters. Tetrahedron,2002:58:3323-3328.
33. Schröter S, Stock C, Bach T. Regioselective cross-coupling reactions of multiple halogenated nitrogen-, oxygen-, and sulfur-containing heterocycles. Tetrahedron,2005:61:2245-2267.
34. Fallahpour RA. Carboxylate derivatives of oligopyridines. Synthesis,2000:8:1138-1142.
35. Cruskie MP, Zoltewicz JA, Abboud KA. Revised structure and convergent synthesis of Nemertelline, neurotoxic isolated from the haplonemertine sea worm, quarterpyridine. Journal Organic Chemistry,1995:60:7491-7495.
36. Quallich GJ, Fox DE, Friedmann RC, Murtiashaw CW. Azatetralone synthesis via regioselective Grignard coupling and Parham cyclization. Journal of Organic Chemistry,1992:57:761-764.
37. Connon SJ, Hegarty AF. Stabilised 2,3-Pyridyne Reactive Intermediates of Exceptional Dienophilicity. Europeon Journal of Organic Chemistry,2004:3477-3483.
38. Schnürch M, Spina M, Khan AF, Mihovilovic MD, Stanetty P. Halogen dance reactions-A review. Chemical Society Reviews,2007:36:1046-1057.
39. Marsais F, Quéguiner G. Review on the metallation of π -deficient heteroaromatic compounds: Regioselective ortho-lithiation of 3-fluoropyridine: Directing effects and application to synthesis of 2,3- or 3,4-disubstituted pyridines. Tetrahedron,1983:39:2009-2021.
40. Hart H. Supplement C2, The Chemistry of Triple Bonded Functional Groups. Wiley, Chichester, 1994, 1113.
41. Gros PC, Elaachbouni F. Bromine–lithium exchange under non-cryogenic conditions: TMSCH2Li–LiDMAE promoted C-2 lithiation of 2,3-dibromopyridine. Chemical Communication, 2008, 4813.