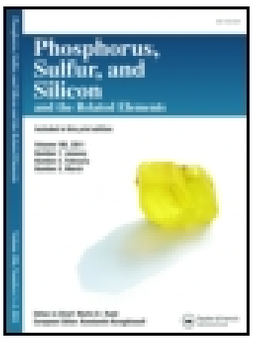

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Synthesis and characterization of unsymmetric 4-picolyl selenides

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ABSTRACT

A number of unsymmetrical heteroaryl 4-picolyl selenides have been prepared by lithiation of 4-picoline using lithium diisopropylamide under cryogenic conditions. The intermediate 4-lithiopicoline formed was then reacted with elemental selenium followed by the addition of suitable electrophiles to give 4-picolyl alkyl selenides. 4-Lithiopicoline was also made to react directly with diaryl/dibenzyl diselenide to yield mixed 4-picolyl aryl/benzyl selenides. All these hitherto unknown selenides were characterized through various spectroscopic techniques viz., NMR (^{1}H, ^{13}C, ^{77}Se), IR and mass spectrometry.

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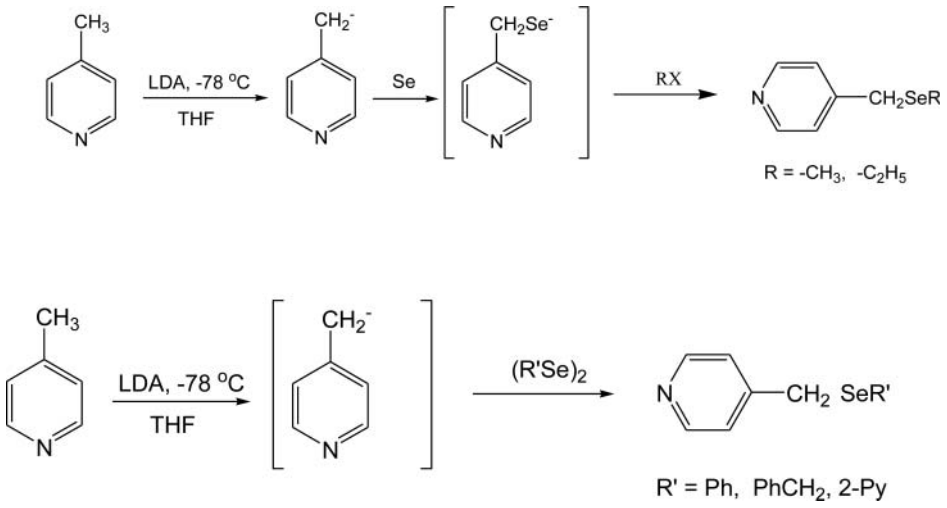
4-Picolyl; phenyl; benzyl; lithium diisopropylamide

GRAPHICAL ABSTRACT



Introduction

Interest in the field of organochalcogenides chemistry has increased over a period of time, as these compounds have become increasingly important as reagents and intermediates in organic synthesis,[1–3] transition metal chemistry,[4] medicinal chemistry,[5] photography,[6] and precursors for metal organic chemical vapor deposition in semiconductor materials.[7] These compounds are used as a mimic of glutathione peroxidase, an enzyme known for its antioxidant properties[8,9] and also have a great role as antimicrobial agents[10] and are known for their anticarcinogenic[11,12] and hyperglycemic[13] properties. Curiously, a literature survey reveals that heteroaryl chalcogenides have not able to keep pace with the advances made in the field of aromatic/aliphatic chalcogenides[14–16] as their synthetic methodologies are time consuming, cumbersome, require expensive reagents and involve drastic conditions.[17–19]

A vast range of bioactive molecules contains the pyridine unit that may be regarded as a pharmacophoric group and an essential building block for biological function. Thus, the development of new strategies for the preparation of this class of compounds has become an important endeavor in synthetic chemistry.[20] Due to lack of systematic study on the chemistry of chalcogen derivatives of 4-picoline, it has not merited special attention in literature.[21–24] Therefore we wish to report a new, efficient and a convenient method for the synthesis and characterization of mixed selenides of 4-picoline.

Results and discussion

Dipyridyl diselenide[18a] has been prepared by lithiation of 2-bromopyridine with *n*-BuLi, subsequent insertion of elemental chalcogen and followed by the aerial oxidation of lithium

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2-pyridyl selenolates. However, a similar attempt to lithiate the methyl moiety of 4-picoline using *n*-BuLi was not successful as it led to the lithiation at C-6 position of pyridine ring. *n*-BuLi in association with tetramethylethylenediamine, leads to a Chichibabin-type reaction that has been documented in the literature.[25] These findings were the driving force to investigate lithium diisopropylamide, a sterically hindered base for the lithiation of 4-picoline to synthesize the orange red colored 4-lithiopicoline. This, on subsequent insertion of selenium at −78°C with continuous stirring until all elemental selenium dissolved, led to the formation of a reddish brown solution of intermediate selenolate, which was used for further reactions.

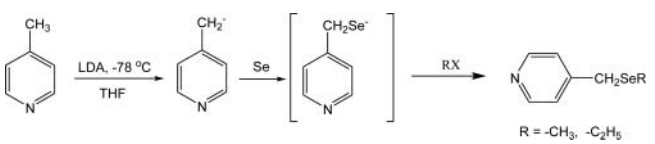
Mixed 4-picolyl alkyl selenides were prepared by the reaction of intermediate selenolate with suitable alkyl halides, viz., methyl iodide and ethyl bromide at −78°C in dried THF. After the addition of alkyl halides at −78°C, the reaction mixture was brought to room temperature with continuous stirring. The progress of the reaction was monitored by TLC till the completion of reaction. After the usual workup and column chromatography on silica gel using hexane-ethyl acetate (9:1, v/v) as eluent, pure 4-picolyl alkyl selenides were obtained (Scheme 1).

Unsymmetrical 4-picolyl alkyl selenides, prepared by the aforementioned methodology, are yellow viscous foul smelling liquids and are stable at room temperature. 4-Picolyl selenides are less stable as compared to the corresponding alkyl/aryl compounds. However, these compounds are comparable in stability with respect to mixed 2-picolyl selenium compounds. These compounds are miscible in conventional organic solvents such as diethyl ether, chloroform, dichloromethane and were characterized through various spectroscopic techniques, viz., NMR (^{1}H, ^{13}C, ^{77}Se), IR and mass spectrometry in representative cases.

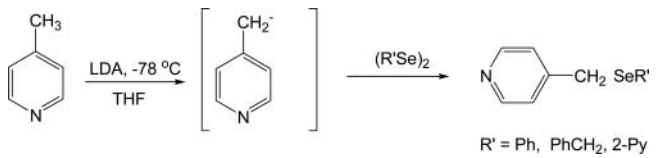
Infrared spectra of these mixed 4-picolyl alkyl selenides were recorded in KBr plates in the range 4000–400 cm^{-1}. Bands in the region 3100–3000 and 1600–1400 cm^{-1} have been assigned to C-H and C=C, C=N stretching vibrations of pyridine ring whereas those in the range 2900–2800 cm^{-1} correspond to C-H stretching mode of methyl, methylene groups and 600–400 cm^{-1} bands signify C-Se stretching vibrations. ^{1}H NMR spectra of these selenides obtained in $CDCl_3$ using TMS as an internal reference, display two sets of signals, one corresponding to aliphatic protons of methyl, methylene groups in the range 1.27–3.61 (δ, *ppm*) and other to the aromatic protons of pyridine ring appearing in the region between 7.06 and 8.44 (δ *ppm*). ^{13}C NMR spectra of these compounds in $CDCl_3$ as a reference solvent, display aromatic carbon signals in the range 122.2–149.9 (δ, *ppm*) due to magnetically nonequivalent carbon atoms of the pyridyl ring whereas aliphatic carbon signals for the methyl and methylene groups appear in the region 4.1–26.4 (δ, *ppm*). Fragmentation pattern in the mass spectrum of representative compound, 4-picolyl ethyl selenide follows the path that involves the loss of different groups to form various species, M+1 peak at *m/z* 202 $[C_8H_{13}NSe]^{+\cdot}$(62) and other peaks are at *m/z* 172 $[C_6H_6NSe]^{+\cdot}$ (58), *m/z* 93 $[C_6H_7N]^{+}$ (100).

Unsymmetrical selenides were also prepared by the cleavage of selenium-selenium bond in diaryl/dibenzyl diselenide with 4-lithiopicoline. Diaryl/dibenzyl diselenides undergo a reaction with 4-lithiopicoline at −78°C in dried THF to form aryl/benzyl selenolate, which further react with 4-lithiopicoline to afford mixed 4-picolyl aryl/benzyl selenides in excellent yields. It was observed that if the addition of diaryl/dibenzyl diselenide occur in one installment, the desired selenide formed was in very low yield, but slow addition of diaryl/dibenzyl diselenide solution in dried THF resulted in high yields of mixed 4-picolyl aryl/benzyl selenides (Scheme 2).

All these newly synthesized unknown unsymmetrical selenides are liquids with a foul odor, soluble in organic solvents such as diethyl ether, chloroform, and dichloromethane. The compounds were characterized through various spectroscopic techniques, viz., NMR (^{1}H, ^{13}C, ^{77}Se), IR and mass spectrometry in representative cases. ^{1}H NMR spectra of these mixed selenides in $CDCl_3$ using TMS as an internal reference display aromatic protons signals in the range 6.86–8.40 (δ *ppm*) whereas methylene protons signals appear in 3.47–4.31 (δ, *ppm*) region. It was observed that methylene protons attached to the pyridine ring appear downfield compared to the methylene protons attached to phenyl ring in benzyl group due to the deshielding effect of nitrogen in the pyridine ring. Methylene protons appear more downfield when both the rings are pyridine as in the case of 4-picolyl 2-pyridyl selenide due to the presence of two electronegative nitrogen atoms in the rings. ^{13}C NMR spectra of these unsymmetrical selenides display aromatic carbon signals in 120.6–154.2 (δ, *ppm*) range whereas aliphatic carbon signals for methylene groups appear in the region 25.7–30.4 (δ, ppm). ^{77}Se NMR spectra of the representative mixed 4-picolyl aryl/benzyl selenides with dimethyl selenide as an external reference reveals that the ^{77}Se resonance signals are very sensitive to even small variation of substituents attached to selenium as substituents affect the polarizability of electron cloud of relatively soft selenium atom. ^{77}Se chemical shift values in 4-picolyl 2-pyridyl selenide and 4-picolyl benzyl selenide were obtained at 418.7 (δ, ppm) and 338.2 (δ, ppm). The downfield shift of value in the former case is due to the attachment of selenium to the pyridine ring, whereas in the latter case selenium is bonded to benzylic carbon of the benzyl group. Mass spectra of these unsymmetrical selenides contain signals corresponding to number of characteristic ions, which confirm their structures. As a representative example, the fragmentation pattern of 4-picolyl 2-pyridyl selenide displays the M+1 peak at m/z 251 $[C_{11}H_{11}N_2Se]^{+\cdot}$ (13) and other fragments appear at *m/z* 170 $[C_{11}H_{10}N_2]^{+}$ (100), 169 $[C_{11}H_9N_2]^{+}$ (42), 93 $[C_6H_7N]^{+}$ (12).



Scheme 1. Preparation of 4-picolyl alkyl selenides.



Scheme 2. Preparation of mixed 4-picolyl aryl/benzyl selenides.

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In an effort to extend the above methodology to prepare mixed tellurium compounds of 4-picoline, the intermediate tellurolate was prepared by insertion of elemental tellurium to 4-lithiopicoline. Quenching of intermediate tellurolate with methyl iodide did not afford expected telluride, but resulted in the formation of dimethyl ditelluride as evidenced by ^{1}H NMR. A plausible mechanism for the reaction has been demonstrated in Scheme 3.

Hydrolysis of intermediate selenolate/tellurolate followed by its aerial oxidation did not yield the desired 4,4'-dipicolyl diselenide, but resulted in the complete decomposition of the reaction mixture, which led to the formation of the coupled product, viz., 1,2-*bis*(4-pyridyl)ethane in quantitative yield.

Experimental

All synthetic reactions were carried out under a dry and inert nitrogen atmosphere to prevent oxidation of the oxygen-sensitive selenium/tellurium intermediates. Elemental selenium/tellurium (sigma Aldrich) were activated and stored in a vacuum desiccator over anhydrous $CaCl_2$. THF was freshly dried and distilled over sodium-benzophenone prior to use. 4-Picoline (Fluka) and diisopropylamine (Fluka) were dried and distilled over KOH pallets. Diphenyl diselenide/ditelluride,[26] dibenzyl diselenide,[27] and dipyridyl diselenide[18] were prepared by reported methods. ^{1}H, ^{13}C, and ^{77}Se NMR spectra were recorded on JEOL AL 300 MHz and BRUKER II 400MHz spectrometers in solvents CCl_4/$CDCl_3$ using Me_4Si (TMS) as an internal standard for ^{1}H and ^{13}C NMR, whereas ^{77}Se NMR spectra were recorded with Me_2Se as an external reference. IR spectra were recorded between KBr plates on a Perkin Elmer model 1430 ratio recording spectrometer. Mass Spectra (EI, 70 eV) were obtained on VG-705 11–250J and WATERS Q-TOF MICRO mass spectrometers. Separation and purification were carried out by column chromatography using silica gel of 100–200 mesh and eluted with mixture of suitable solvents. Sample ^{1}H, ^{13}C and ^{77}Se NMR spectra for 3 are shown in the Supplemental Materials (Figures S1–S3).

General procedure for the preparation of unsymmetrical 4-picolyl alkyl selenides

To a solution of intermediate selenolate, obtained from 4-picoline (0.48 g, 5.2 mmol), diisopropylamine (0.34 g, 6.1 mmol), *n*-BuLi (0.18 mL, 6.1 mmol), and elemental selenium (0.48 g, 6.05 mmol) at –78°C under an inert atmosphere of nitrogen, was added the suitable electrophiles (methyl iodide 0.8 g; 5.6 mmol, ethyl bromide, 0.61 g; 5.6 mmol) dissolved in dried THF (3.0 mL) drop wise to the reaction mixture. After the addition at −78°C, the reaction mixture was brought to room temperature with continuous stirring. The progress of the reaction was monitored by TLC. On completion of the reaction, the reaction mixture was extracted with dichloromethane (3 × 20 mL) and washed with water. The solvent was dried over anhydrous sodium sulfate and evaporated under reduced pressure to afford crude product. It was then subjected to column chromatography on silica gel using hexane-ethyl acetate (9:1, v/v) as eluent yielded following unsymmetrical 4-picolyl alkyl selenides.

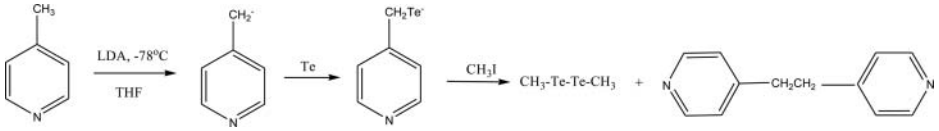
4-Picolyl methyl selenide, ($C_5H_4NCH_2SeCH_3$)**,** [1]: Yellow viscous liquid, Yield: 60% ; ^{1}H NMR (300 MHz, $CDCl_3$/TMS, 25°C) : δ, 1.81 (*s*, 3H), 3.55 (*s*, 2H), 7.06–7.08 (*d*, 2H, J = 5.7 Hz), 8.39–8.41 (*d*, 2H, J = 5.7 Hz); ^{13}C NMR ($CDCl_3$/TMS): δ, 4.1(-CH_3), 26.4($PyCH_2$), 122.2(C-5), 123.5(C-3), 147.8(C-4), 149.5(C-6), 149.7(C-2); ^{77}Se NMR: δ, 179.7; IR (KBr, cm^{-1}): 3390, 2922, 2054, 1599, 1557,1415,1276, 1067, 922, 834, 813, 621, 554, 470; MS (EI, %): 188 $[C_7H_{10}NSe]^+$ (36); 172 $[C_6H_7NSe]^+$ (12); 107 $[C_2H_3Se]^+$ (9); 93 $[C_6H_7N]^+$ (100).

4-Picolyl ethyl selenide, ($C_5H_4NCH_2SeCH_2CH_3$)**,** [2]: Yellow viscous liquid, Yield: 72%; ^{1}H NMR (300 MHz, $CDCl_3$/TMS, 25°C) : δ, 1.27–1.33 (*t*, 3H, J = 7.5 Hz, J = 7.5 Hz), 2.37–2.51 (*q*, 2H), 3.61 (*s*, 2H), 7.10–7.12 (*d*, 2H, J = 4.8 Hz),8.44 (*bs*, 2H); ^{13}C NMR ($CDCl_3$/TMS): δ, 15.2(Se-CH_2), 17.6 (CH_3), 25.1($PyCH_2$), 123.8(C-3,C-5), 148.5(C-4), 149.8(C-6), 149.9(C-2); ^{77}Se NMR: δ, 196.8; IR (KBr, cm^{-1}): 3399, 2956, 2923, 2056, 1598, 1448, 1413, 1375, 1233, 1066, 991, 831, 812, 734, 620, 553, 470; MS (EI, %): 202 $[C_8H_{12}NSe]^+$ (62); 172 $[C_6H_6NSe]^+$ (58); 93 $[C_6H_7N]^+$ (100).

General method for the synthesis of mixed 4-picolyl aryl/benzyl selenides

To solution of 4-lithiopicoline, obtained from 4-picoline (0.48 g, 5.2 mmol), diisopropylamine (0.34 g, 6.1 mmol) and *n*-BuLi (0.18 mL, 6.1 mmol), prepared at −78 °C under an inert atmosphere of nitrogen, 5.2 mmoles of dipyridyl/diphenyl/dibenzyl diselenide, dissolved in dried THF was added drop wise over a period of 1 h. The reaction mixture was brought to room temperature slowly with continuous stirring till the completion of the reaction. Usual workup of the reaction mixture, followed by column chromatography purification on silica gel yielded following pure unsymmetrical selenides in nearly quantitative yields.

4-Picolyl 2-pyridyl selenide, ($C_5H_4NCH_2SeC_5H_4N$), [3]: Yellow viscous liquid; yield: 80%; ^{1}H NMR (300 MHz, $CDCl_3$/TMS, 25°C): δ 4.31 (*s*, 2H), 6.94–6.98 (*m*, 1H), 7.16–7.18 (*m*, 3H), 7.32–7.35 (*m*, 1H), 8.36–8.40 (*t*, 3H, J = 6.0 Hz, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$/TMS): δ, 27.2 ($PyCH_2Se$), 121.7, 124.0, 125.3, 127.9, 136.6, 148.8, 149.7, 150.1, 154.2; ^{77}Se NMR: δ, 418.7; IR (KBr, cm^{-1}): 3409, 2959, 2927, 1722, 1598, 1573, 1557, 1449, 1413, 1380, 1278, 1147, 1108, 1042, 986, 810, 755, 699, 623, 554, 467; MS (EI, %): 251 $[C_{11}H_{11}N_2Se]^+$ (13); 170 $[C_{11}H_{10}N_2]^+$ (100); 169 $[C_{11}H_9N_2]^+$ (42); 93 $[C_6H_7N]^+$ (12).



Scheme 3. Mechanistic Pathway for the formation of dimethyl ditelluride.

4-Picolyl phenyl selenide, ($C_5H_4NCH_2SeC_6H_5$), [4]: Yellow viscous liquid, yield: 70%; ^{1}H NMR (300 MHz, $CDCl_3$/TMS, 25°C): δ, 3.82 (*s*, 2H), 6.86–6.88 (*d*, 2H, J = 4.8 Hz), 7.07–7.14 (*m*, 3H), 7.26–7.28 (*d*, 2H, J = 8.0 Hz), 8.29–8.31 (*d*, 2H, J = 5 Hz); ^{13}C NMR ($CDCl_3$/TMS): δ, 30.4 ($PyCH_2$), 123.3, 127.6, 128.8, 134.0, 147.4, 149.4; ^{77}Se NMR: δ, 365.5; IR (KBr, cm^{-1}): 3399, 3067, 1598, 1577, 1558, 1476, 1436, 1413, 1067, 832, 810, 738, 691, 670, 611, 552, 464; MS (EI, %): 250 $[C_{12}H_{12}NSe]^+$ (61); 169 $[C_{12}H_{11}N]^+$ (20); 93 $[C_6H_7N]^+$ (100).

4-Picolyl benzyl selenide, ($C_5H_4NCH_2SeCH_2C_6H_5$), [5]: Yellow viscous liquid, yield: 62%; ^{1}H NMR (300 MHz, $CDCl_3$/TMS, 25°C): δ, 3.47 (*s*, 2H), 3.61 (*s*, 2H), 7.01 (*s*, 2H), 7.13–7.17 (*m*, 5H), 8.38 (*s*, 2H); ^{13}C NMR ($CDCl_3$/TMS): δ, 25.7 ($PhCH_2$), 27.7 ($PyCH_2$), 123.8, 126.9, 128.5, 128.9, 138.2, 148.1, 149.7; ^{77}Se NMR: δ, 338.2; IR (KBr, cm^{-1}): 3390, 3026, 2925, 2853, 1721, 1599, 1557, 1493, 1453, 1415, 1279, 1214, 1179, 1067, 1029, 992, 912, 812, 759, 698, 610, 552, 470; MS (EI, %): 264 $[C_{13}H_{14}NSe]^+$ (100); 170 $[C_7H_6Se]^+$ (28); 93 $[C_6H_7N]^+$ (63).

Conclusions

In summary, the present studies provide a new, convenient and an efficient protocol for the synthesis of unknown mixed organyl selenides *via* the reaction of intermediate selenolate with suitable electrophiles and by the cleavage of selenium-selenium bond in diaryl/dibenzyl diselenide with 4-lithiopicoline, as previously reported synthetic methods suffer due to their lengthy synthetic procedures, harsh reaction conditions and expensive reagents.

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