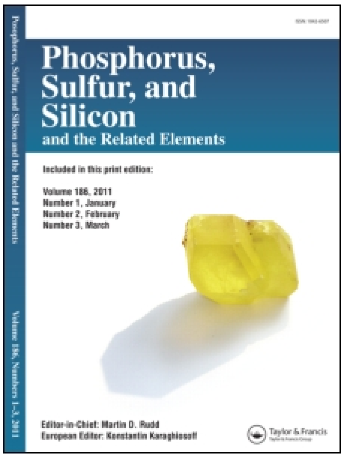

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PREPARATION AND CHARACTERIZATION OF 2,2′-DIPICOLYL DISELENIDE AND THEIR DERIVATIVES

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Lithium 2-picolylselenolate/tellurolate is obtained by reacting lithiated 2-picoline with elemental selenium/tellurium which upon aerial oxidation gives 2,2′-dipicolyl diselenide in case of selenium while 1,2-bis(2-pyridyl)ethane in case of tellurium. Condensation of 2-picolylselenolate anion with a variety of electrophiles provides a facile synthesis of 2-picolylalkyl selenides in good to excellent yields. Quenching of lithiated 2-picoline with 2,2′-dipyridyl diselenide gives mixed 2-picolylseleno pyridine in low yield. All the compounds prepared are new and have been characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR and mass spectral studies.

INTRODUCTION

Organic compounds of selenium and tellurium have attracted recently considerable interest as reagents and intermediates in organic synthesis,[1–4] biochemistry,[5] photography,[6] and precursors for metal organic chemical vapour deposition (MOCVD) in semiconductor materials.[7] Compared to chemistry of pyridylselenium/tellurium compounds,[8–13] we have not encountered any reference on the preparation of 2-picolylselenium/tellurium derivatives. In continuation of our work on the chemistry of selenium and tellurium compounds,[14,15] we wish to report for the first time a new and convenient method for the preparation and characterisation of the hitherto unknown relatively less stable titled organoselenium compounds starting from 2-picoline.

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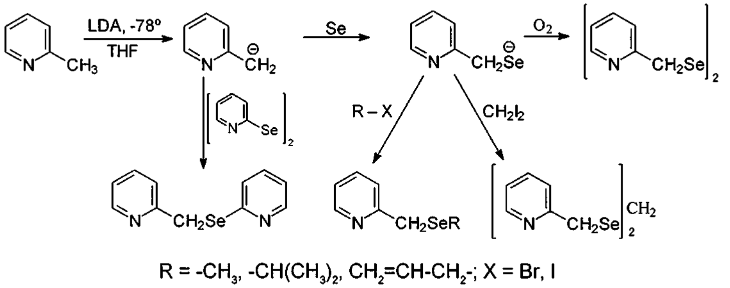
RESULTS AND DISCUSSION

Lithiation of 2-picoline has conveniently been achieved by the slow addition of 2-picoline to a well stirred solution of lithium diisopropylamide in THF at −78°C as a burgundy red solution.[16] Addition of elemental selenium/tellurium to the homogeneous suspension of 2-picoline anion at −78°C affords the corresponding lithium 2-picolyl selenolate/tellurolate, which can be directly used for further reactions. It is important to note that selenium dissolves completely within 20 minutes whereas it takes nearly 45 min to dissolve elemental tellurium. This is probably because, the commercially available tellurium is known to exhibit low chemical reactivity due to its surface oxidation.[17]

Aerial oxidation of the solution of lithium 2-picolylselenolate as obtained above resulted in the formation of 2,2′-dipicolyl diselenide in excellent yield (see Scheme 1). ^{1}H NMR spectrum of 2,2′-dipicolyl diselenide in $CDCl_3$ shows that the ring protons (8H) appear at 8.53–7.04 (δ ppm) and the benzylic signal (4H) centers at 4.05 (δ ppm). An interesting feature of 2,2′-dipicolyl diselenide is its photochemical lability. It is important to note that the yield always improves when the reaction is carried out in the presence of red light. However, exposure of the chloroform or acetone solution of 2,2′-dipicolyl diselenide to ordinary ceiling lights leads to the appearance of black elemental selenium in the solution. ^{1}H NMR spectrum of the solution, after removing elemental selenium, reveals that the ring protons appear at nearly the same position whereas benzylic signal is shifted upfield 3.93 (δ ppm). Elemental analysis combined with other spectroscopic studies corresponds to the formation of 2,2′-dipicolyl selenide.



R = $-CH_3$, $-CH(CH_3)_2$, CH_2=CH-CH_2-; X = Br, I

SCHEME 1 Methodology for 2-picolylselenium derivatives.

Aerial oxidation of the lithium 2-picolyltellurolate is accompanied by the complete decomposition of the resulting product as is evidenced by the total recovery of elemental tellurium. Analysis of the decomposed solution revealed quantitatively the formation of the coupled product viz; 1,2-bis(2-pyridyl)ethane. Several reactions were carried out to control the decomposition of 2,2′-dipicolyl ditelluride by employing different reaction conditions but all were met with total decomposition of the tellurium product.

Several unsymmetrical 2-picolylalkyl selenides were prepared by adding THF solution of iodomethane, 2-bromopropane, 3-bromo-prop-2-ene, and diiodomethane to the solution of lithium 2-picolyl selenolate at −78°C.

Lithiated 2-picoline upon quenching with 2,2′-dipyridyl diselenide affords unsymmetrical 2-picolylseleno pyridine (see Scheme 1) in low yield. All the newly prepared 2-picolyl derivatives of selenium are golden yellow oils with mild odor. The physical and spectroscopic data of these compounds are presented in Table I.

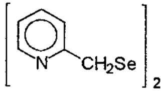
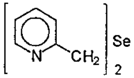
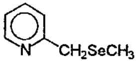
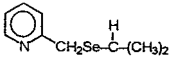
EXPERIMENTAL

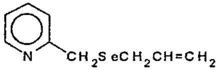
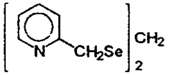
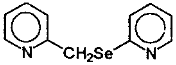
All manipulations were carried out under a dry nitrogen atmosphere to prevent oxidation of the oxygen-sensitive selenium/tellurium intermediates. 2-Picoline (Sisco), iodomethane (Sisco), 2-bromopropane (Sisco), 3-bromopropene (Sisco), and diiodomethane (Lancaster) were dried and distilled under nitrogen before use. 2,2′-Dipyridyl diselenide was prepared by the literature method.[9] NMR spectra were recorded in $CDCl_3$ using TMS as internal standard on Bruker AC-300F, 300 MHz spectrometer. Mass spectra (El, 70 eV) were obtained on a VG Analytical 11-2505-70 SMS mass spectrometer. Carbon, hydrogen and nitrogen were estimated microanalytically using Perkin-Elmer 2400 CHN Elemental Analyzer. Selenium was estimated by standard methods.[18]

General Method for the Preparation of Lithium 2-picolylselenolate/tellurolate

In a clean, flame dried two-necked round bottom flask was placed 2.4 ml (24.3 mmol) of diisopropylamine in tetrahydrofuran. The solution was cooled to 0°C to which 24.3 mmol of *n*-BuLi was added dropwise. The solution was allowed to stir for 20 min and then cooled to −78°C. Dropwise addition of 2-picoline, 2 ml (22.2 mmol) was made slowly. The solution turned from colourless to red. Stirring was continued for an additional 30 min. Elemental selenium 1.9 g. (24.3 mmol) was added at −78°C, the reaction mixture was slowly brought to room temperature till all the elemental selenium dissolves. The reaction mixture was hydrolysed

TABLE I Physical and Spectroscopic Data of 2-picolylselenium Compounds

Compound	Yield (%)	^{1}H NMR (δ ppm) CDCl$_3$/TMS	^{13}C NMR (δ ppm) CDCl$_3$/TMS	m/e	Assignment
	60–70	8.53–8.50 (d, 2H) 7.62–7.55 (m, 2H) 7.14–7.04 (m, 4H) 4.05 (s, 4H)	159.5, 149.5, 136.4, 123.1, 121.8, 29.8	344 264 252 184 172 93 78	$(C_6H_6NSe)^{+}{}_2$ $[(C_6H_6N)_2Se]^+$ $(C_6H_6NSe_2)^+$ $(C_6H_6N)_2{}^+$ $C_6H_6NSe^+$ $C_6H_7N^+$ $C_5H_4N^+$
	—	8.54–8.49 (d, 2H) 7.61–7.55 (m, 2H) 7.32–7.30 (d, 2H) 7.15–7.07 (m, 2H) 3.93 (s, 4H)	159.5, 149.1, 137.0, 123.0, 121.5, 29.0	264 184 172 93 78	$[(C_6H_6N)_2Se]^+$ $(C_6H_6N)_2{}^+$ $C_6H_6NSe^+$ $C_6H_7N^+$ $C_5H_4N^+$
	85	8.50–8.49 (d, 1H) 7.63–7.57 (m, 1H) 7.31–7.26 (d, 1H) 7.16–7.09 (m, 1H) 3.84 (s, 2H) 1.98 (s, 3H)	159.9, 149.1, 136.5, 123.1, 121.5, 29.9, 4.4	187 172 93 78	$C_7H_9NSe^+$ $C_6H_6NSe^+$ $C_6H_7N^+$ $C_5H_4N^+$
	82	8.54–8.50 (d, 1H) 7.63–7.58 (m, 1H) 7.34–7.29 (d, 1H) 7.16–7.08 (m, 1H) 3.95 (s, 2H) 3.18–3.09 (m, 1H) 4.42–1.39 (d, 6H)	159.6, 149.1, 136.5, 123.1, 121.3, 29.3, 17.9, 17.5	215 172 93 78	$C_9H_{13}NSe^+$ $C_6H_6NSe^+$ $C_6H_7N^+$ $C_5H_4N^+$

	85	8.50–8.48 (d, 1H) 7.59–7.54 (t, 1H) 7.26–7.23 (d, 1H) 7.09–7.05 (d, 1H) 5.94–5.80 (m, 1H) 5.10–4.99 (q, 2H) 3.82 (s, 2H) 3.22–3.16 (d, 2H)	159.2, 148.8, 135.9, 134.1, 122.5,120.9, 16.2, 27.8, 25.6	213 172 121 93 78	$C_9H_{11}NSe^+$ $C_6H_6NSe^+$ $C_3H_5Se^+$ $C_6H_7N^+$ $C_5H_4N^+$
	82	8.58–8.56 (d, 2H) 7.67–7.64 (t, 2H) 7.41–7.38 (d, 2H) 7.21–7.17 (m, 2H) 4.47 (s, 2H) 4.20 (s, 4H)	159.2, 148.3, 135.7, 122.5, 120.1, 29.8, 15.6	358 344 264 184 172 93 78	$(C_6H_6NSe)_2CH_2{}^+$ $(C_6H_6NSe)_2{}^+$ $(C_6H_6N)_2Se^+$ $(C_6H_6N)_2{}^+$ $C_6H_6NSe^+$ $C_6H_7N^+$ $C_5H_4N^+$
	20	8.52–8.47 (q, 2H) 7.56–7.53 (m, 1H) 7.45–7.35 (m, 3H) 7.09–7.01 (m, 2H) 4.58 (s, 2H)	159.5, 155.1, 150.3, 149.6, 136.6, 136.0, 125.7, 125.3, 122.2, 121.7, 30.8	250 172 93 78	$C_{11}H_{10}N_2Se^+$ $C_6H_6NSe^+$ $C_6H_7N^+$ $C_5H_4N^+$

with 20 ml of water and the supply of nitrogen was discontinued. The reaction mixture was exposed to aerial oxidation for 30 min when a clear yellow solution was obtained. The product was extracted with diethyl ether (3 × 20 ml) and the filtrate was dried over anhydrous sodium sulphate. The solvent was evaporated on the rota-evaporator. The crude product was subjected to column chromatography on silica gel using hexane-ethyl acetate (10:1) as eluent to obtain pure 2,2′-dipicolyl diselenide (see Table I for spectral values) in good yield as golden yellow viscous oil with mild odour.

In a separate experiment, lithium-2-picolyltellurolate was obtained exactly as above, which upon aerial oxidation resulted in the formation of the coupled product 1,2-bis(2-pyridyl) ethane.

Preparation of 2,2′-dipicolyl Selenide

A solution of 2,2′-dipicolyl diselenide (250 mg.) in chloroform or acetone (0.5 ml) was irradiated in the presence of nitrogen, using a Hanovia lamp, for nearly 40 min and the reaction product left over after the removal of elemental selenium was subjected to column chromatography using hexane and ethyl acetate as eluent to afford pure 2,2′-dipicolyl selenide (see Table I for spectral values).

Preparation of Unsymmetrical 2-picolyl Selenides

To a solution of 2-picolylselenolate at −78°C, as prepared above in a flame-dried flask under nitrogen, the appropriate electrophile (iodomethane, diiodomethane, 3-bromoprop-2-ene, and 2-bromopropane) in THF was added dropwise. The reaction mixture was warmed to room temperature with continuous stirring. The progress of the reaction was monitored by TLC. On completion of the reaction, the mixture was washed with water and extracted with diethyl ether (3 × 20 ml). The filtrate was dried over anhydrous sodium sulphate and the solvent evaporated to afford the analytically pure 2-alkylpyridyl selenides (see Table I for spectral values).

Preparation of 2-picolyl Selenopyridine

To a solution of lithiated 2-picoline (10.0 mmol) at −78°C, as prepared above in a flame dried flask under nitrogen, 3.16 g (10.0 mmol) of 2,2′-dipyridyl diselenide in THF was added dropwise over a period of 30 min. The reaction mixture was brought to room temperature slowly with continuous stirring. The color of the solution initially turned from red to yellow and after some time it again turned red. The reaction mixture was worked up as usual to afford pure 2-picolyl selenopyridine in low yield (See Table I for spectral values).

In summary, the present one flask procedure provides a new protocol for the synthesis of hitherto unknown 2,2′-dipicolyl diselenide and some of its derivatives in good yields for the first time and constitutes an important addition to the synthetic methodology in view of the simple operation and good yields.

ACKNOWLEDGMENT

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