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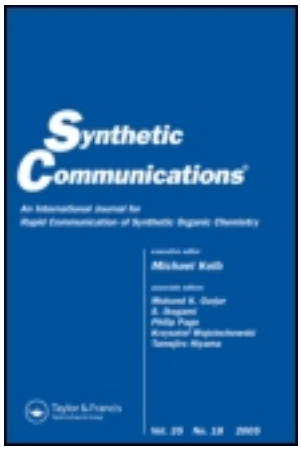

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A NEW AND CONVENIENT ROUTE TO 2,2′-DIPYRIDYL DISELENIDE/DITELLURIDE AND SOME OF THEIR ALKYL/ARYL DERIVATIVES THROUGH BF_3-COMPLEXED PYRIDYL CARBANION

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SYNTHETIC COMMUNICATIONS, 32(9), 1319–1325 (2002)

A NEW AND CONVENIENT ROUTE TO 2,2′-DIPYRIDYL DISELENIDE/ DITELLURIDE AND SOME OF THEIR ALKYL/ARYL DERIVATIVES THROUGH BF_3-COMPLEXED PYRIDYL CARBANION

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ABSTRACT

Synthesis of 2,2′-dipyridyl diselenide/ditelluride and some alkyl/aryl pyridyl selenide/telluride is reported.

Key Words: Chalcogens; Organic; Selenium; Tellurium; Pyridine

Organoselenium and organotellurium compounds have become increasingly important as reagents and intermediates in organic synthesis[1,2] apart from proving promising donor molecules for conductive[3] and photoconductive organic molecules.[4] Although there exists a variety of methods for the introduction of selenium/tellurium into organic molecules, research continues on the development of new selenium or tellurium transfer reagents and methods.[5,6] It is curious to note that compared to the chemistry of alkyl, aryl or mixed alkyl aryl chalcogenides, the corresponding chemistry of pyr-

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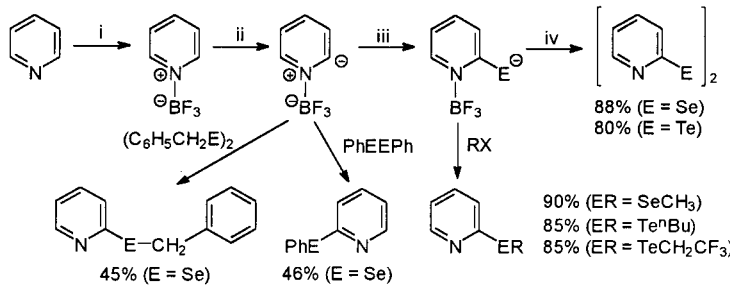
idyl chalcogenides has not been developed. In continuation of our work,[7,8] on the chemistry of organoselenium and organotellurium compounds, we wish to report a new and convenient method for the preparation of 2,2′-dipyridyl diselenide/ditelluride and some of their 2-pyridyl selenium/tellurium derivatives.

It has recently been reported by two of us[9,10] that deprotonation of BF_3-complexed pyridine can be conveniently accomplished at the 2-position **1** with the highly hindered base lithium tetramethyl piperidine (LTMP) in ether at $-78^{\circ}C$. The usefulness of the methodology has now been extended towards the preparation of several versatile pyridyl selenium/tellurium compounds which are not only difficult to prepare in respectable yields but also require longer hours. Elemental selenium/tellurium when added to the BF_3-complexed 2-lithiopyridine solution at $-78^{\circ}C$ and allowing the reaction to come to room temperature affords a deep red coloured solution **2** with the complete dissolution of metals. Elemental selenium dissolves readily in 20 min whereas elemental tellurium takes about 45 min to dissolve almost completely. It is probably because the commercially available tellurium is known to exhibit low chemical reactivity due to its surface oxidation.[11]

Aerial oxidation of **2** after usual work up affords 2,2′-dipyridyl diselenide/ditelluride in nearly quantitative yields. The present method for the preparation of 2,2′-dipyridyl diselenide has several advantages over the existing methods in terms of easy work up and requires only 2 h compared to 23–92 h reported in the literature.[14] In addition it avoids the use[14a] and in situ evolution[14c] of highly toxic hydrogen selenide gas. Whereas in case of 2,2′-dipyridyl ditelluride it gives maximum yield when compared to reported methods.[15]

Alkylation of the deep red coloured solution of BF_3-complexed 2-seleno/telluropyridyl carbanion solution **2** as prepared above was carried



Scheme. Methodology for the synthesis. Reagents and conditions: i) $BF_3{\cdot}Et_2O$, $0^{\circ}C$, 15 min, ether, ii) LTMP, $-78^{\circ}C$, 15 min, ether, iii) $E = Se/Te$, $-78^{\circ}C$, 30 min. iv) hydrolysis and aerial oxidation at room temperature for 30 min.

out by a variety of alkylating agents at $-78^{\circ}C$. After warming to about $-20^{\circ}C$, and allowing to come to room temperature followed by usual work up afforded high yields of alkyl pyridyl selenide/telluride indicating clearly that lithium 2-pyridyl selenolate/tellurolate or a chemically equivalent specie is cleanly formed when elemental selenium/tellurium reacts with 2-lithiated pyridine. This procedure describes the preparation of 2-methylselenopyridine and 2-(*n*)-butyltelluropyridine starting from cheaply and conveniently available pyridine. It requires less time with better yields and compares favourably with those reported in the literature starting from 2-bromopyridine. [14(a,b),16,17]

Quenching of the BF_3-complexed lithiated 2-pyridine **1** with diphenyl diselenide and dibenzyl diselenide resulted in the reductive cleavage of heteroatom-heteroatom bond with the formation of phenylpyridyl selenide and benzyl pyridyl selenide respectively in good yields.

EXPERIMENTAL

All manipulations must be carried out under a dry oxygen-free nitrogen atmosphere to prevent the oxidation of oxygen sensitive selenium and tellurium intermediates.

Elemental selenium and tellurium was stored in a desiccator prior to use. Diphenyl diselenide[12] and dibenzyl diselenide[13] was prepared by the literature methods. Methyl iodide (Sisco) *n*-butyl bromide (Sisco) and 2,2,2-trifluoroethyl iodide (Aldrich), were purified by distillation and were subsequently deoxygenated with a stream of nitrogen. The ^1H NMR spectra were recorded in $CDCl_3$, relative to TMS using a Varian EM 390 operated at 90 MHz.^{13}C NMR spectra were recorded on Jeol FX90Q FT NMR spectrometer operating at 22.49 MHz with an internal deuterium lock. Infrared spectra were recorded as neat liquid between AgCl plates on a Perkin-Elmer 1430 spectrophotometer. The EI mass spectra were obtained on a VG 705, 11-2503 mass spectrometer at 70 eV. C, H and N were estimated on a Perkin-Elmer 2400 CHN elemental analyzer.

General Procedure for the Generation of BF_3-Complexed 2-Pyridyl Seleno/Telluro Carbanion Followed by the Aerial Oxidation for the Preparation of 2,2′-Dipyridyl Diselenide/Ditelluride

Into a flame dried two necked round bottomed flask equipped with a stir bar and septum cap was placed a solution of pyridine (0.23 g, 0.24 ml,

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3.0 mmol) in dry ether (15 ml) under oxygen-free nitrogen atmosphere. The solution was cooled to 0°C in ice bath, and $BF_3{\cdot}Et_2O$ (0.46 g, 0.41 ml, 3.3 mmol) added to it. The resulting white suspension was stirred at 0° for 15 min. The temperature was lowered to −78°C and LTMP (Lithium tetramethyl piperidine), prepared by stirring TMP (0.46 g, 0.56 ml, 3.3 mmol) in dry ether (10 ml) and *n*-BuLi (2.2 ml, 1.5 N, 3.3 mmol) at −10°C, was added slowly via cannula under nitrogen atmosphere. The resulting brown solution was stirred for 15 min at −78°C. Elemental selenium/tellurium (3.0 mmol) was added and temperature was raised slowly until complete dissolution of selenium/tellurium took place. At this stage the supply of nitrogen was discontinued and the reaction mixture was hydrolyzed followed by exposing to aerial oxidation for 30 min. The aqueous layer was extracted with diethyl ether (4 × 10 ml), organic layer was washed with water, brine and dried over anhydrous sodium sulphate. The solvent was removed on a rotary evaporator to afford the crude product which was purified by column chromatography as yellow needles in case of 2,2′-dipyridyl diselenide and as red crystals in case of 2,2′-dipyridyl ditelluride.

2,2′-Dipyridyl diselenide: (88% yield) m.p. 48–49°C (lit.[14] 48°C). ^{1}H NMR ($CDCl_3$) δ 6.95 (m, 2H), 7.41 (m, 2H), 7.69 (m, 2H), 8.34 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 120.6, 122.8, 136.7, 148.8 and 153.6. MS (EI): *m*/*z* 316 (M^+); 236 (M^+-Se).

2,2′-Dipyridyl ditelluride: (80% yield) m.p. 51–52°C (lit.[15] 50–51.5°C). ^{1}H NMR ($CDCl_3$) δ 7.02–8.02 (m, 6H), 8.45 (d, 2H). MS (EI): *m*/*z* 416 (M^+); 286 (M^+-Te).

General Procedure for the Preparation of 2-Alkylseleno/Telluropyridine

Alkyl halide {methyl iodide, *n*-butyl bromide or 2,2,2-trifluoroethyl iodide (3.0 mmol)} was added dropwise over a period of 30 min to the cooled solution of BF_3-complexed seleno/telluro pyridyl carbanion (3.0 mmol) at −78°C prepared as described above. After stirring further for 20 min at −78°C, the temperature was gradually allowed to rise to room temperature and quenched with deoxygenated water (20 ml). The aqueous layer was extracted with diethyl ether (4 × 10 ml). The organic layer was washed with water, brine and dried over anhydrous sodium sulphate. The solvent was removed on a rotary evaporator to afford the crude product which was purified by column chromatography/vacuum distillation to afford analytically pure 2-alkylseleno/telluro pyridine.

2-Methylselenopyridine: Pale yellow oil (90% yields), b.p. 50–52°C/30 torr (lit.[16a] 43–44°C/25 mm torr). ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3H),

6.9 (m, 1H), 7.4 (m, 1H); 7.2 (m, 1H); 8.4 (m, 1H). MS (EI): m/z 173 (M^+); 93 (M^+-Se).

2-(*n*)Butyltelluoropyridine:[17] Yellow oil (85% yield). ^{1}H NMR ($CDCl_3$) δ 0.92–0.89 (m, 3H), 1.46–1.41 (m, 2H), 1.93–1.88 (m, 2H), 3.15–3.10 (t, 2H); 6.99–6.97 (m, 1H), 7.30–7.29 (m, 1H), 7.45–7.39 (m, 1H), 8.47–8.46 (d, 1H). ^{13}C NMR ($CDCl_3$) δ 9.28, 13.4, 25.1, 1, 33.8, 120.8, 131.5, 135.2, 141.1 and 150.6. MS (EI): m/z 265 (M^+); 135 (M^+-Te).

2,2,2-Trifluoroethyltelluoropyridine: Light yellow oil (85% yield). ^{1}H NMR ($CDCl_3$) δ 4.10–3.7 (q, 2H), 7.50–7.39 (m, 3H), 8.61–8.60 (d, 1H). ^{19}F NMR δ 58.5 (t, CH_2CF_3). IR (neat): 3060, 2976, 2928, 1631, 1590, 1568, 1472, 1432, 1290, 1260, 1246, 1151, 1050, 990, 863, 575, 537, 461 cm^{-1}. MS (EI): m/z 291 (M^+); 161 (M^+-Te). Anal. calcd for $C_7H_6NF_3Te$: C, 28.86; H, 2.06; N, 4.81. Found: C, 28.72; H, 2.01; N, 4.92.

General Procedure for the Preparation of 2-Phenylselenopyridine

Diphenyl diselenide (3.0 mmol) dissolved in 20 ml THF was added dropwise over a period of 20 min to the cooled solution of BF_3-complexed 2-pyridyl carbanion (3.0 mmol) at −78°C as described above in the typical preparation. After stirring for 20 min at −78°C, the temperature was gradually allowed to rise to room temperature and quenched with deoxygenated water (20 ml). It was subjected to usual work up as described above and afforded the crude product, which was purified by flash chromatography to give analytically pure 2-phenylselenopyridine in 46% yield as pale yellow oil.[16a] ^{1}H NMR δ 7.0–6.8 (m, 2H), 7.4–7.1 (m, 4H), 7.70–7.50 (m, 2H), 8.4–8.26 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 120.2, 124.0, 127.5, 128.6, 129.4, 135.9, 136.4, 149.6 and 158.5. MS (EI) 234 (M^+); 154 (M^+-Se).

2-Benzylselenopyridine: 2-Benzylselenopyridine was prepared similarly using dibenzyl diselenide. It was purified by column chromatography over silica gel. Elution with hexane–ethylacetate (8 : 2) afforded the pure viscous oil in 45% yield. ^{1}H NMR δ 4.4 (s, 2H); 7.0–7.6 (m, 8H), 8.4–8.6 (d, 1H), ^{13}C ($CDCl_3$) δ 29.2, 120.4, 125.3, 126.8, 128.4, 128.9, 135.9, 139.0, 149.9, 155.5. IR (neat): 3080, 3060, 2969, 2938, 1637, 1571, 1556, 1453, 1437, 1260, 1034, 982, 808, 503, 470 cm^{-1}. MS (EI) 249 (M^+); 168 (M^+-SeH). Anal. calcd for $C_{12}H_{11}NSe$: C, 57.83; H, 4.41; N, 5.62. Found: C, 57.75; H, 4.23; N, 5.60.

In summary, the present one flask procedure provides a new path for the synthesis of 2,2′-dipyridyl diselenide/ditelluride and their derivatives and constitutes an important addition to the synthetic methodology starting from pyridine. In addition, it has advantages of mild conditions, simple operation and good yields over the existing methods in the literature.

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