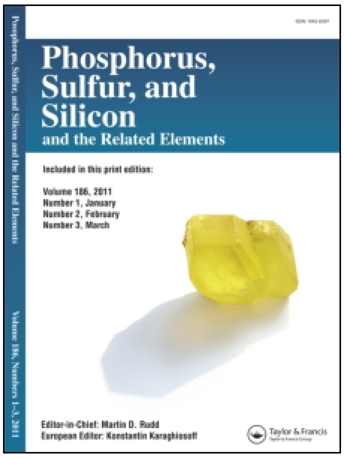

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An Insight into the Reductive Cleavage of Tellurium-Tellurium Bond in Various 2,2'-Dipyridyl Ditelluride Using Hydrazine Hydrate

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AN INSIGHT INTO THE REDUCTIVE CLEAVAGE OF TELLURIUM-TELLURIUM BOND IN VARIOUS 2,2′-DIPYRIDYL DITELLURIDE USING HYDRAZINE HYDRATE

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Reductive cleavage of tellurium-tellurium bond in various 2,2′-dipyridyl ditellurides using hydrazine hydrate (100%) both in the presence and absence of phase transfer catalyst is reported. A tentative mechanism of the reaction is also proposed.

Keywords: Chalcogens; hydrazine hydrate; tellurides; tellurium

The chemistry of alkyl, aryl, and mixed alkyl aryl tellurium compounds has long been an interesting topic because of its synthetic applications in organic synthesis[1–3] and potential application in MOCVD.[4] However, the corresponding pyridyltellurium chemistry, although equally useful[5] has received far less attention and remained underexplored. The primary reason for this is attributed to lack of efficient and convenient methods for the synthesis of these compounds. We have successfully developed efficient and convenient methods for the synthesis of various methyl-substituted[7] and unsubstituted[8] pyridyl chalcogen derivatives as part of our studies on the chemistry of 2,2′-dipyridyl ditellurides. We report our detailed results on the reductive cleavage of tellurium-tellurium bond in various 2,2′-dipyridyl ditellurides with hydrazine hydrate (100%) in highly basic media for the preparation of symmetrical and unsymmetrical 2-pyridyl tellurides.

Dedicated to the loving memories of Professor R. C. Paul (1919–2002).

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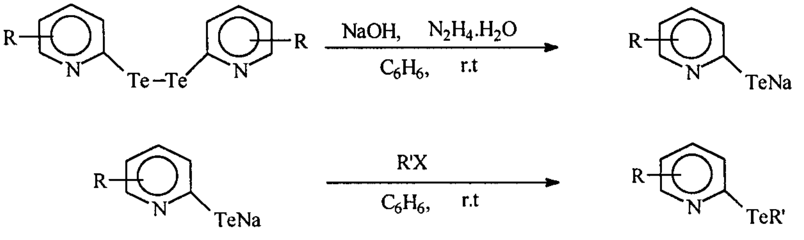
RESULTS AND DISCUSSION

Syper and Mlochowski[9] were the first to explore the reductive nature of the hydrazine hydrate for the cleavage of selenium-selenium bond in dimethyl and diphenyl diselenide. It is important to mention that the reductions were carried out in the presence of phase-transfer catalyst in aprotic solvents viz., benzene, tetrahydrofuran, and pentane. During the course of our studies, it was thought that the cleavage of tellurium-tellurium bond in various 2,2′-dipyridyl ditellurides could be achieved with hydrazine hydrate (100%) even without the phase-transfer catalyst. The main consideration for this approach was the water affinity of the pyridine moiety. Our approach was vindicated when dark red solution of 2,2′-dipyridyl ditellurides in THF changed to pale yellow upon treatment with hydrazine hydrate in the presence of highly basic media indicating the formation of 2-pyridyl tellurolate anion. The anion then reacts readily with various alkyl and allyl halides to give the desired compounds (1–4) in good yields (Scheme 1).

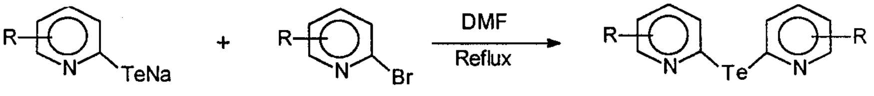


($R= CH_3$ or H)

(X= Br, I) (R' = Me, isopropyl, butyl, allyl)

SCHEME 1 Synthesis of unsymmetrical 2-alkyl/allyltelluro pyridines.

The reaction of 2-pyridyl tellurolate anion with the corresponding 2-bromopyridine in THF was not successful. However, the same reaction in DMF yielded the desired 2,2′-dipyridyl tellurides in good to moderate yields (Scheme 2).



($R= CH_3$ or H)

R= 4-Me (5)
R= 4-Me & 5-Br (6)
R= 3-Me (7)

SCHEME 2 Synthesis of symmetrical 2,2′-dipyridyl tellurides.

TABLE I Effect of PEG-400 on the Yield of 2-Methyltelluro-5-Picoline

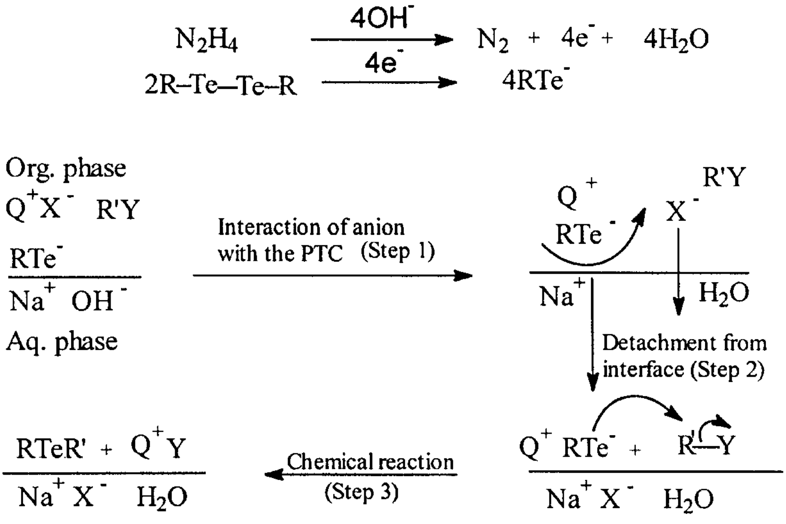
Entry	Reagent	Solvent	PTC	T/h	Yield %
1	$(5\text{-MePyTe})_2$, NaOH, $N_2H_4 \cdot H_2O$	C_6H_6	PEG-400	1	82
2	$(5\text{-MePyTe})_2$, NaOH, $N_2H_4 \cdot H_2O$	C_6H_6	None	2	73

In order to study the effect of phase-transfer catalyst on the efficiency of these reactions, the above reactions were carried out in the presence of phase-transfer catalyst viz. polyethyleneglycol-400, tetrabutylammonium bromide, tetrabutylammonium chloride, and benzyltriethylammonium bromide. However, it was observed that the presence of phase-transfer catalyst marginally increases the yield of the reaction (Table I). Thus, it appears that the phase-transfer catalyst may not be involved in the production of the tellurolate anion and only catalyzes the substitution reaction with various electrophiles.

As part of our studies, we also examined the solvent effect on the efficiencies of these reactions employing different solvents, such as benzene, THF, pentane, and hexane. The efficiency of the reaction in various solvents is in the following order:

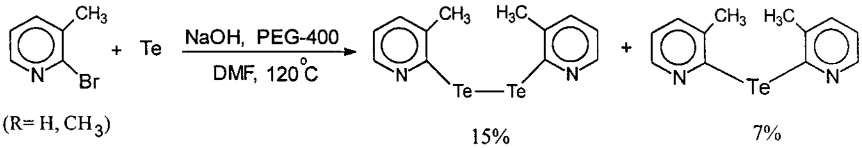
$$\text{benzene} > \text{THF} > \text{pentane} = \text{hexane}$$

On the basis of our experimental findings, a tentative interfacial mechanism for the above reaction is proposed in the Scheme 3.



SCHEME 3 Interfacial mechanism for the phase transfer reaction.

In order to further explore the potential of hydrazine hydrate, we attempted to synthesize 3,3′-dimethyl 2,2′-dipyridyl tellurides by the reduction of elemental tellurium in DMF with hydrazine hydrate in the presence of NaOH, followed by the treatment of the resulting species with 2-bromo-3-methyl pyridine. However, to our surprise we got both 3,3′-dimethyl 2,2′-dipyridyl ditelluride and -telluride in low yields (Scheme 4) indicating the formation of Na_2Te_2 and Na_2Te, which is contrary to the earlier report.[10]



SCHEME 4 Use of hydrazine hydrate (100%) for the synthesis of 3,3′-dimethyl-2,2′-dipyridyl ditelluride and -telluride.

All the compounds prepared are foul smelling viscous oil except **7** and **8**. All these tellurides have tendency to decompose in solution and require immediate work-up. This is probably the reason for the low yields of these compounds compared to the corresponding selenides.[7]

CONCLUSION

The present work presents a convenient approach towards the synthesis of various pyridyltellurium compounds, which otherwise require controlled experimental conditions and longer time period.[5,7]

EXPERIMENTAL

All experiments were carried out in dry oxygen-free nitrogen atmosphere. The melting points reported are uncorrected. Infrared spectra were recorded in CCl_4 on a Perkin-Elmer Model 1430 ratio recording spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on Bruker AC-300F, 300 MHz spectrometer. The mass spectra were obtained on a VG-705 11-250J Mass spectrometer. Carbon, hydrogen, and nitrogen were estimated micro-analytically on Perkin-Elmer 2400 CHN elemental analyzer. All the 2-bromopyridines were prepared from the corresponding 2-aminopyridines (Lancaster) by employing Craig's method.[11]

General Method for the Preparation of Unsymmetrical 2-Alkyl/allyltelluro Pyridines

To a vigorously stirred mixture of powdered sodium hydroxide (0.25 g, 62.5 mmol), 2,2′-dipyridyl ditelluride (12 mmol), and aprotic solvent (40 ml), 100% hydrazine hydrate (0.1 ml, 4 mmol) was added dropwise at room temperature. Stirring was continued for additional 30 min. A solution of electrophile in THF was added slowly at 0°C. After completion of the reaction, as evidenced by TLC, the solvent was removed and the residue was treated with water and extracted with dichloromethane (4 × 50 ml). The extract was dried over anhydrous sodium sulfate and the solvent removed on a rota-evaporator. The residue was purified by column chromatography using silica gel and hexane-ethylacetate as eluent (10:1).

2-Methyltelluro-5-picoline (1): Yield 82% [7]. ^{1}H NMR: δ, 2.10 (s, 3H), 2.35 (s, 3H), 7.05–7.15 (m, 2H), 8.05 (s, 1H). ^{13}C NMR: δ, 5.37, 17.6, 123.8, 129.2, 136.5, 150.0, 151.8. IR (Neat, cm^{-1}): 3053, 2955, 2928, 1562, 1435, 1262, 665, 546, 467. Anal. Calcd. for: C_7H_9NTe; C, 35.80, H, 3.84, N, 5.96. Found: C, 35.87, H, 4.07, N, 5.25.

2-(n)-Butyltelluro-pyridine (2): Yield 76% [5, 8]. ^{1}H NMR: δ, 0.89–0.92 (m, 3H), 1.41–1.46 (m, 2H), 1.88–193 (m, 2H), 3.10–3.15 (t, 2H), 6.97–6.99 (m, 1H), 7.30–7.29 (m, 1H), 7.39–7.45 (m, 1H), 8.46–8.47 (d, 1H). ^{13}C NMR: δ, 9.28, 13.42, 25.18, 33.81, 120.83, 131.55, 135.23, 141.10, 150.65. IR (Neat, cm^{-1}): 3040, 2910, 2850, 1620, 1590, 1451, 1370, 1083, 616, 539, 467. Anal. Calcd. for: $C_9H_{13}NTe$; C, 41.12, H, 4.95, N, 5.33. Found: C, 40.32, H, 4.38, N, 5.12.

2-Isopropyltelluro-5-picoline (3): Yield 73%. ^{1}H NMR: δ, 1.58–1.64 (d, 6H), 2.15 (s, 3H), 3.70–3.80 (m, 1H), 7.05–7.15 (m, 2H), 8.05 (s, 1H). ^{13}C NMR: δ, 17.58, 17.90, 26.63, 130.75, 132.83, 136.25, 137.20, 151.25. IR (Neat, cm^{-1}): 3025, 2963, 2908, 1637, 1573, 1443, 1383, 723, 685, 634, 467. MS (EI): 265 [M ^{130}Te]$^+$ (18.4); 223 [M-CH(CH$_3$)$_2$]$^+$ (55.3); 135 [M-Te] (20.7); 92 [M-TeCH(CH$_3$)$_2$]$^+$ (100). Anal. Calcd. for: $C_9H_{13}NTe$; C, 41.22, H, 4.22, N, 5.37. Found: C, 41.13, H, 4.54, N, 5.61.

2-Allyltelluro-3-picoline (4): Yield 62%. ^{1}H NMR: δ, 2.19 (s, 3H), 3.94–3.96 (d, 2H), 4.79–4.83 (d, 1H), 5.07–5.13 (d, 1H), 6.07–6.18 (m, 1H), 6.88–6.93 (m, 1H), 7.10–7.13 (d, 1H), 8.31–8.32 (d, 1H). ^{13}C NMR: δ, 12.28, 21.44, 114.60, 120.03, 134.96, 136.71, 137.01, 147.48, 148.13. IR (Neat, cm^{-1}): 3043, 2977, 2928, 1633, 1571, 1451, 1346, 539, 467. Anal. Calcd. for: $C_9H_{11}NTe$; C, 41.24, H, 4.22, N, 5.37. Found: C, 40.17, H, 4.16, N, 5.39.

General Method for the Preparation of Symmetrical 2,2′-Dipyridyl tellurides

To a vigorously stirred mixture of powdered sodium hydroxide (0.25 g, 62.5 mmol), 2,2′-dipridyl ditelluride (12 mmol), and DMF (40 ml), 100% hydrazine hydrate (0.1 ml, 4 mmol) was added dropwise at room temperature. Stirring was continued for additional 30 min. A solution of corresponding 2-bromopyridine in THF was added slowly and the resulting solution was refluxed for 24 h. After completion of the reaction as evidenced by TLC, the solvent was removed and the residue was treated with water and extracted with dichloromethane (4 × 50 ml). The extract was dried over anhydrous sodium sulfate and the solvent removed on a rota-evaporator. The residue was purified by column chromatography using silica gel and hexane-ethylacetate as eluent (5:1).

4,4′-Dimethyl-2,2′-dipyridyl telluride (5): Yield, 62% semisolid. ^{1}H NMR: δ, 2.27 (s, 6H), 6.90–6.92 (d, 2H), 7.56 (s, 2H), 8.35–8.37 (d, 2H). ^{13}C NMR: δ, 20.85, 124.05, 132.06, 135.70, 148.17, 150.23. IR (KBr, cm^{-1}): 3023, 2969, 2917, 1654, 1582, 1544, 1451, 1261, 1368, 694, 520, 473. Anal. Calcd. for: $C_{12}H_{12}N_2Te$; C, 46.21, H, 3.85, N, 8.98. Found: C, 46.17, H, 3.72, N, 8.76.

5,5′-Dibromo-4,4′-dimethyl-2,2′-dipyridyl telluride (6): Yield, 65% m.p. 106–107°C. ^{1}H NMR: δ, 2.31 (s, 6H), 7.87 (s, 2H), 8.47 (s, 2H). ^{13}C NMR: δ, 21.45, 122.52, 128.02, 132.50, 140.41, 159.24. IR (KBr, cm^{-1}): 3035, 2925, 2908, 1685, 1579, 1552, 1450, 1361, 635, 473. ME (EI): 472 [M ^{130}Te]$^+$ (2.1); 342 [M-Te]$^+$ (12.1); 302 [M-BrC_6H_4N] (13.1), 172 [M-BrC_6H_4NTe]$^+$ (100); 90 [M-$Br_2C_6H_6NTe$]$^+$ (100). Anal. Calcd. for: $C_{12}Br_2H_{10}N_2Te$; C, 30.66, H, 2.12, N, 5.96. Found: C, 30.85, H, 2.05, N, 6.18.

3,3′-Dimethyl-2,2′-dipyridyl telluride (7): Yield, 52%, ^{1}H NMR: δ, 2.10 (s, 6H), 6.89–6.96 (t, 2H), 7.22–7.24 (m, 2H), 8.20–8.24 (d, 2H). ^{13}C NMR: δ, 20.47, 119.03, 133.67, 135.92, 138.02, 146.51. IR (KBr, cm^{-1}): 3045, 2940, 2920, 1577, 1540, 1430, 1357, 685, 473. ME (EI): 314 [M^{130}Te]$^+$ (13.01); 222 [M-C_6H_6N]$^+$ (4.8); 183 [M-TeH]$^+$ (46.62); 92 [M-C_6H_6NTe]$^+$ (100). Anal. Calcd. for: $C_{12}H_{12}N_2Te$; C, 46.21, H, 3.85, N, 8.98. Found: C, 46.13, H, 3.71, N, 8.70.

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