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Ring Expansion Reaction of 1,3-Dithiolanes and 1,3-Oxathiolanes Using Tellurium Tetrachloride

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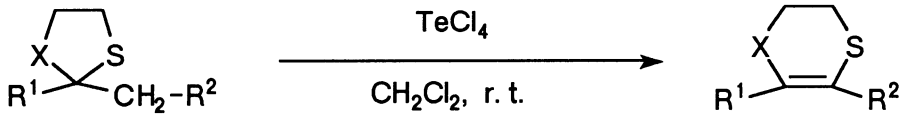
On treatment with tellurium tetrachloride in dichloromethane at room temperature, 1,3-dithiolanes and 1,3-oxathiolanes undergo smooth ring expansion to give dihydro-1,4-dithiin and dihydro-1,4-oxathiin derivatives respectively in good to moderate yields.

Acetals and dithioacetals are easily cleaved with tellurium tetrachloride ($TeCl_4$) to regenerate original carbonyl compounds.[1] When this procedure was applied to cyclic dithioacetals, a facile ring enlargement by one carbon atom occurred via the 1,2-migration of sulfur atom. Based on this finding, we now report a convenient one-step synthesis of 1,2-disubstituted 5,6-dihydro-1,4-dithiins (**3**) and 5,6-dihydro-1,4-oxathiins (**4**) from 2,2-disubstituted 1,3-dithiolanes (**1**) and 1,3-oxathiolanes (**2**), respectively, using $TeCl_4$ as a mild Lewis acid oxidant.



X = S (**1**)
X = O (**2**)

X = S (**3**)
X = O (**4**)

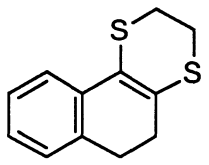
On treatment with an equimolar amount of $TeCl_4$ in dichloromethane at room temperature, 1,3-dithiolanes (**1**) underwent smooth ring expansion to give dihydro-1,4-dithiins (**3**) in 49-99% yields (Table 1). The reaction was clean and no polymeric materials were formed. Dithiolanes derived from cyclic ketones furnished better results than those from open chain ketones. Reaction of 1-tetralone ethylenedithioacetal (**1h**) was rather unexpected, since it was accompanied by extensive aromatization of the initial product to give naphtho[1,2-b]dihydro-1,4-dithiin (**5**). In acetonitrile, however, the dihydro derivative (**3h**) was obtained as a sole product. Compound **3h** was found to be stable in open air, so the nascent tellurium or tellurium dichloride ($TeCl_2$) may be

responsible as dehydrogenating agent for aromatization.

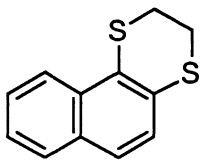
Table 1. Dihydro-1,4-dithiins (3) and dihydro-1,4-oxathiins (4) obtained

Product[a]	R^1	R^2	X	Yield / %[b]
3a	C_6H_5-	H-	S	49
3b	C_6H_5-	CH_3-	S	58
3c	C_6H_5-	C_6H_5-	S	99
3d	$C_6H_5CH_2$-	C_6H_5-	S	62
3e	-$(CH_2)_4$-		S	82
3f[8]	-(1,2-C_6H_4)-CH_2-		S	89
3g[8]	-(1,2-C_6H_4)-$C(CH_3)_2$-		S	99
3h[8]	-(1,2-C_6H_4)-$(CH_2)_2$-		S	60[c]
4a	C_6H_5-	C_6H_5-	O	39[d]
4b	-$(CH_2)_4$-		O	36[d]
4c[8]	-(1,2-C_6H_4)-$C(CH_3)_2$-		O	27[d]
5[8]	-(1,2-C_6H_4)-CH=CH-		S	85[e]

a) All compounds are known unless otherwise mentioned. New compounds were characterized by elemental microanalyses as well as mass, IR, ^1H and ^{13}C NMR spectra.
b) Yields refer to the isolated compounds and are not optimized.
c) The reaction was carried out in acetonitrile.
d) Parent ketone was another important product.
e) The reaction was carried out in benzene.



3h



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Dichloromethane, chloroform, carbon tetrachloride, and benzene were the solvent of choice. Acetonitrile was less satisfactory. When THF, ether or hexane was used, the reaction was incomplete. $TeCl_4$ was reduced during this transformation and recovered as elementary tellurium by simple filtration.

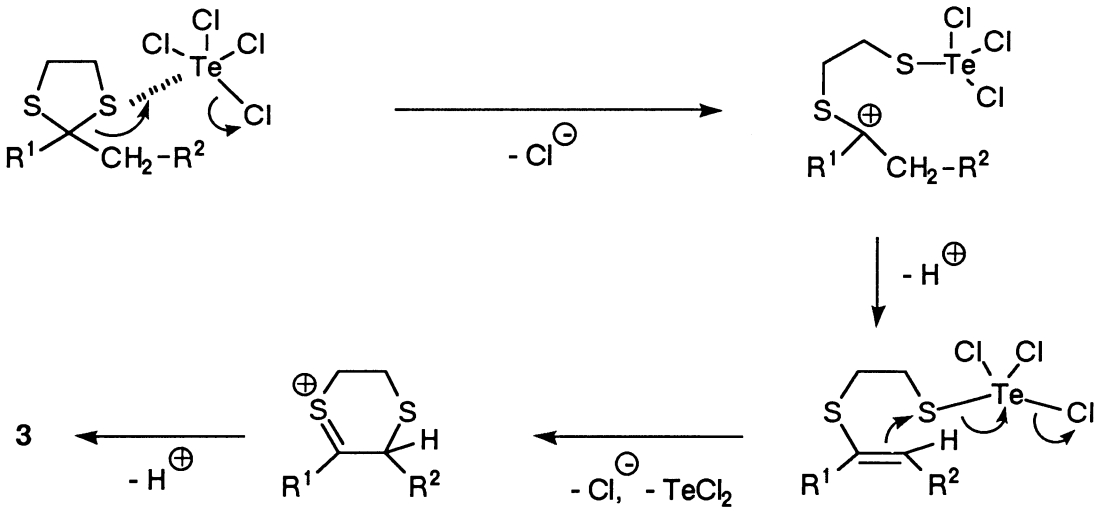
The general procedure was as follows: To a solution of 1,3-dithiolane (1.0 mmol) in dichloromethane (10 ml) was added powdered $TeCl_4$ (1.1 mmol) and the resulting suspension was stirred for 30 min at room

temperature. During the course of this period, free tellurium separated as a black precipitate. The reaction was quenched by the addition of 5% aqueous sodium hydrogencarbonate and the insoluble material was removed by filtration. The organic layer was separated, dried over sodium sulfate and evaporated under reduced pressure to leave a crude product, which was purified by chromatography on silica gel to give dihydro-1,4-dithiin.

Similar treatment of 1,3-oxathiolanes (**2**) with $TeCl_4$ afforded dihydro-1,4-oxathiins (**4**) in moderate yields. In this case cleavage of hetero ring leading to parent ketones was an important competing reaction, which inevitably lowered the yields of ring expansion products.

A literature survey revealed several precedents of this type of reaction. Treatment of 1,3-dithiolanes with N-chlorocarbamates[2] or phenylselenenyl chloride[3] afforded dihydro-1,4-dithiins. In the former case ring expansion was often accompanied by chlorination and yields were moderate. The latter procedure needed chromatographic purification to remove diphenyl diselenide. Ring expansion of 1,3-oxathiolanes was previously carried out by chlorination with molecular chlorine[4,5] or sulfuryl chloride[6] at low temperatures. Yields were low to moderate and chlorination was significant with the latter reagent.

The $TeCl_4$-mediated rearrangement of 1,3-dithiolanes to dihydro-1,4-dithiins may be depicted as follows. $TeCl_2$ is known to disproportionate easily to Te and $TeCl_4$.[7]



$TeCl_4$ is an easily handled stable solid, commercially available at moderate price. The major advantages of our procedure over the previous ones[2-6] are mild reaction conditions, cleanness of reaction, simplicity of performance, and improvement in yields.

References

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8) Physical properties of new compounds are as follows:
3f: mp 66-67 °C; ^{1}H NMR($CDCl_3$) δ=3.28-3.35(4H, m), 3.48(2H, s), 7.09-7.36(4H, m); ^{13}C NMR($CDCl_3$) δ=25.96, 27.40, 42.32, 116.61, 122.79, 123.43, 124.20, 126.52, 127.36, 139.56, 143.81; MS(70 eV) m/z(rel intensity) 206(M^+; 94), 178(100), 146(25), 134(100). Found: C, 63.95; H, 4.89%. Calcd for $C_{11}H_{10}S_2$: C, 64.04; H, 4.89%.
3g: mp 54-56 °C; ^{1}H NMR($CDCl_3$) δ=1.29(6H, s), 3,26-3.34(4H, m), 7.10-7.29(4H, m); ^{13}C NMR($CDCl_3$) δ=25.22, 26.17, 27.00, 52.04, 116.82, 119.68, 120.40, 124.42, 126.64, 138.69, 141.26, 150.92; MS(70 eV) m/z(rel intensity) 234(M^+; 100), 191(85), 173(56), 147(45), 115(41). Found: C, 66.72; H, 6.04%. Calcd for $C_{13}H_{14}S_2$: C, 66.62; H, 6.02%.
3h: mp 56-57 °C; ^{1}H NMR($CDCl_3$) δ=2.32-2.38(2H, m), 2.74-2.80(2H, m), 3.17-3.27(4H, m), 7.04-7.20(3H, m), 7.40(1H, d, J=7.3 Hz); ^{13}C NMR($CDCl_3$) δ=27.42, 28.17, 29.84, 31.46, 119.08, 121.58, 125.79, 126.18, 126.42, 127.05, 134.11, 134.40; MS(70 eV) m/z(rel intensity) 220(M^+;100), 192(100), 160(44), 128(100). Found: C, 65.43; H, 5.51%. Calcd for $C_{12}H_{12}S_2$: C, 65.41; H, 5.49%.
4c: mp 73-74 °C; ^{1}H NMR($CDCl_3$) δ=1.29(6H, s), 3.09-3.12(2H, m), 4.45-4.48(2H, m), 7.10-7.35(4H, m); ^{13}C NMR($CDCl_3$) δ=25.07, 25.09, 47.54, 66.25, 115.79, 116.58, 120.53, 124.50, 126.52, 128.29, 137.11, 144.30, 150.67; MS(70e V) m/z(rel intensity) 218(M^+; 100), 190(25), 175(28), 162(18), 147(31). Found: C, 71.29; H, 6.52%. Calcd for $C_{13}H_{14}OS$: C, 71.52; H, 6.46%.
5: mp 57-58 °C; ^{1}H NMR($CDCl_3$) δ=3.31-3.41(4H, m), 7.20(1H, d, J=8.9 Hz), 7.38-7.53(3H, m), 7.73(1H, d, J=7.9 Hz), 8.14(1H, d, J=7.9 Hz); ^{13}C NMR($CDCl_3$) δ=28.65, 29.93, 122.41, 125.04, 125.35, 126.50, 126.85, 127.05, 128.40, 129.00, 131.48, 132.05; MS(70 eV) m/z(rel intensity) 218(M^+, 100), 190(99), 146(81), 114(48). Found: C, 65.94; H, 4.72%. Calcd for $C_{12}H_{10}S_2$: C, 66.02; H, 4.62%.

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