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CYCLOFUNCTIONALIZATION OF UNSATURATED ALCOHOLS WITH ARYLTELLURIUM TRIHALIDES

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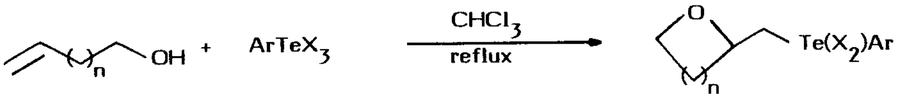
Abstract: The reaction of unsaturated alcohols with aryltellurium trihalides leads to cyclic ethers bearing an aryldihalotelluro group in the β position, in high yields. Reduction of the tellurium-halogen bond with thiourea dioxide gives the corresponding tellurides in excellent yields.

Organic tellurium compounds are emerging as synthetic reagents.[1-3] Aryltellurium trihalides 1 are among the most promising of such reagents in view of their stability and easy preparation. One of the most interesting properties of aryltellurium trihalides is their ability to promote cyclofunctionalizations as demonstrated many years ago when one of us discovered the selenium and tellurium lactonization of unsaturated carboxylic acids.[4,5] Recently we reinvestigated this last reaction in details and studied the properties of the formed dichlorotellurolactones.[6] We found that the product exhibits cis ring fusion.[7] This fact suggests that the cyclization proceeds through a anti addition mechanism. The dichlorotellurolactones can be detellurated either by reaction with tributyl tin hydride, giving tellurium free lactones, or with sodium borohydride giving the starting unsaturated carboxylic acid. Therefore the telluration-detelluration process constitutes a method of protection of γ,δ-unsaturated acids.[6] An extension of this work should be the cyclization of unsaturated alcohols to give cyclic ethers.[8] A recent report of this journal[9] prompted us to disclose our results on this reaction.

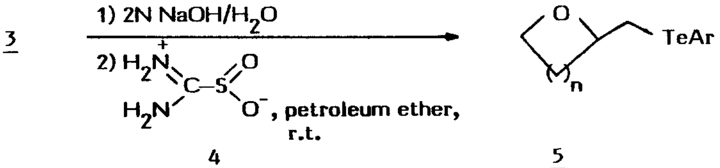
Unsaturated alcohols and phenols 2 react easily with a slight excess of aryltellurium trihalides 1 in chloroform under reflux to give the dichlorotelluro ethers 3 as stable crystalline colorless solids in high yield (Equation 1). When n=1 instead of the cyclic ether the addition product to the double bond was obtained (entry 9, Table 1).



2 1 3

(1)

The products were purified by filtration through a silica gel column eluting with chloroform to remove the excess of aryltellurium trihalide. Recrystallization from chloroform-petroleum ether (30-60) gave the dihalotelluro ethers 3 with the yields given in Table 1. The similar transformation using aryltellurinic anhydrides reported by Ogura and coworkers[9] was performed in acetic acid under reflux leading to diorganyltelluro diacetates in variable yields (15-94%). These products were reported to be hydroscopic and untractable compounds. In some cases the solvent adds to the double bond leading to a mixture of products. On the other hand the reaction time using aryltellurium trihalides is exceedingly short compared with the reaction time of the cyclization using aryltellurinic anhydrides (15 h).[9] We recently found that aminoiminomethane sulfinic acid (thiourea dioxide) 4 is an efficient and selective reducing agent for ditellurides[10], diorganyltelluro dihalides[11] and aryltellurium trihalides.[11] In this work we applied this methodology to the reduction of the cyclization products 3 to the corresponding tellurides 5 (Equation 2).



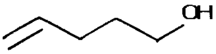
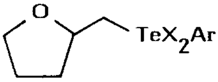
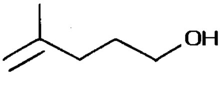
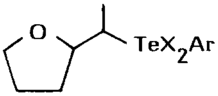
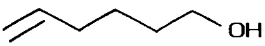
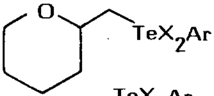
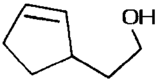
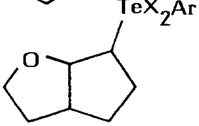
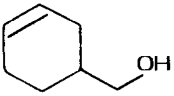
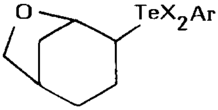
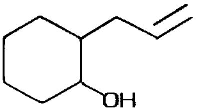
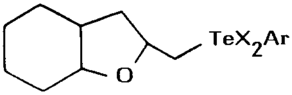
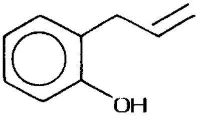
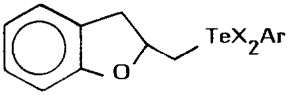
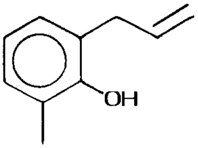
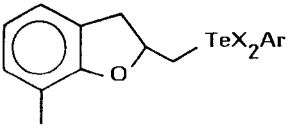
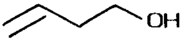
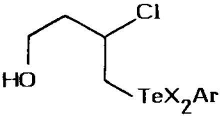
4 5

(2)

The reaction occurs in few minutes at room temperature leading to the products in excellent yields. The reduction of 3 with sodium borohydride in ethanol leads to 5 in lower yields (Table 2). The reduction of the diorganyltelluro diacetates[9] was performed with hydrazine hydrate in ethanol requiring heating at 60°C for 20 min.

The results commented above show that the method developed by us for the tellurocyclofunctionalization of unsaturated alcohols is superior in many aspects to that recently described.[9] This reaction could find use in organic synthesis, since methods to remove tellurium from organic molecules are at the present well established.[3]

Table 1 - Cyclofunctionalization of Unsaturated Alcohols with Aryltellurium Trihalides

	Substrate	Product	Yield (%)[a]	Reaction Time (h)
1.			87^b 93^c 85^d 81^e	0.70 0.17 2.00 12.00
2.			96^b	0.70
3.			93^b	0.70
4.			90^b 86^e	0.50 0.50
5.			78^c	12.00
6.			90^b	0.25
7.			88^b	24.00
8.			71^b	12.00
9.			91^b 85^c	6.00 6.00

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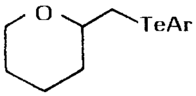
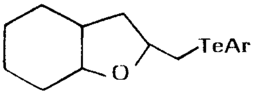
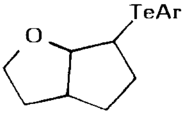
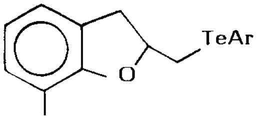
[a] Yield of the recrystalized product. [b] X = Cl; Ar = p-$CH_3OC_6H_4$. [c] X = Cl; Ar = p-$C_6H_5OC_6H_4$. [d] X = Cl; Ar = p-$CH_3C_6H_4$. [e] X = Br; Ar = p-$CH_3OC_6H_4$.

Table 2 - Reduction of the dichlorides 3 to the corresponding tellurides 5

Product	**Yield (%)**	**Reaction Time (h)**
	93[a] 74[b]	0.75 0.7
	95[a] 75[b]	0.75 0.17
	90[a]	0.58
	72[b]	2.00

[a] Thiourea Dioxide/2N NaOH, petroleum ether, r.t.

[b] $NaBH_4$/ethanol, r.t.

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