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REDUCTION OF TELLURIUM - CARBON BONDS OF TELLUROLACTONES AND TELLUROETHERS

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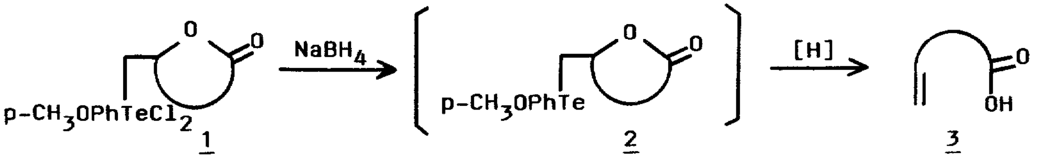
Summary: The lactones and cyclic ethers produced in the tellurocyclofunctionalization of unsaturated carboxylic acids and alcohols are efficiently detellurated by tri-n-butyl tin hydride. Trapping of the intermediate free radicals with methyl acrylate leads to the corresponding adducts in moderate to good yields.

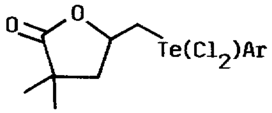
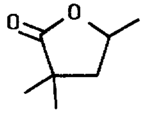
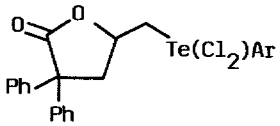
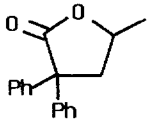
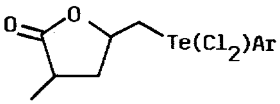
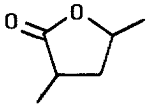
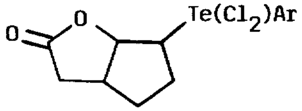
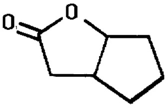
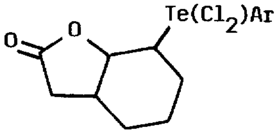
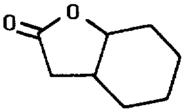
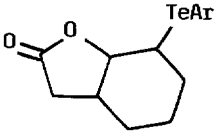
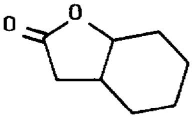
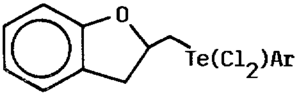
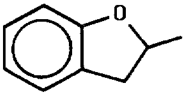
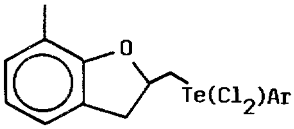
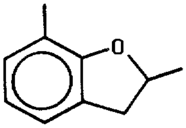
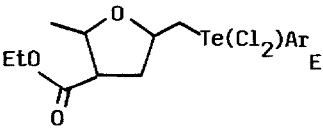
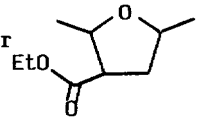
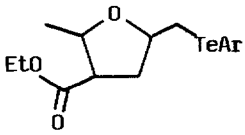
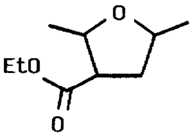
In spite of the growth of organic tellurium chemistry in the last years[1-3], very little work was done aimed at the development of selective methodologies to reduce the tellurium carbon bond.[4] In our search for new synthetic methodologies using tellurium reagents we have prepared aryldichlorotellurolactones (1) by the reaction of unsaturated carboxylic acids with aryltellurium trichlorides[5]. The efficient reductive detelluration of these compounds constitutes a challenge in view of the sensitivity of these systems toward reducing agents. Early attempts to remove tellurium from (1) with sodium borohydride, Raney Ni and n-butyl tin hydride lead to almost quantitative regeneration of the unsaturated carboxylic acid (3) and di-p-methoxy- phenylditelluride[6]. By using only one equivalent of sodium borohydride in ethanol the reduction stops at the telluride stage, furnishing 2 in high yield (Eq. 1)[5].



(1)

In this communication we report that both 1 and 2 can lead to the tellurium free lactone (4) by reaction with tri-n-butyl tin hydride (TBTH) in toluene at reflux, provided the reaction mixture is carefully deoxygenated before the addition of TBTH. A radical initiator was not necessary (Eq. 2, Table 1)[7].

Table 1 - Reduction of tellurolactones and telluroethers with tri n-butyl tin hydride

	Substrate	Product	TBTH (Eq.)	Reaction Time(h)	Yield[a,b] (%)	purity (G.L.C.) (%)
1.			4	4	90	100
2.			4	4	90	100
3.			4	4	92	100
4.			3.3	4	87	100
5.			4	3	92	100
6.			2	2	95	100
7.			4	6	92	99
8.			4	6	90	99
9.			4	8	58	100
10.			2	2	84	100

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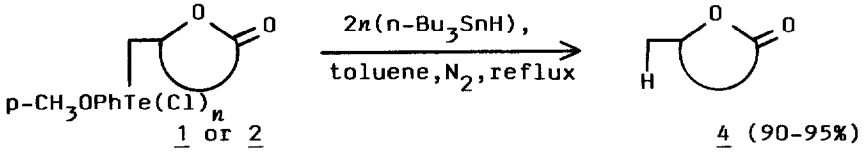
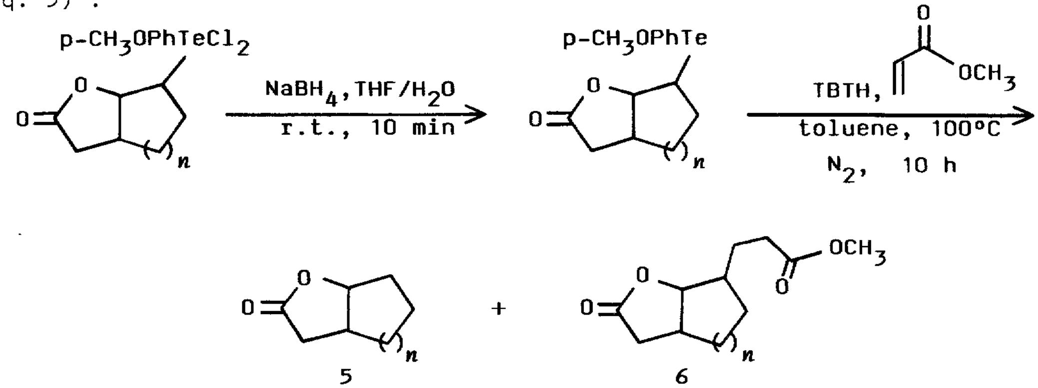
[a] Yield of the isolate products after column chromatography; [b] The spectral data are in accordance with proposed structures. Ar = p-CH_3OPh



(2)

Use of 2 instead of 1 saves two equivalents of TBTH and makes the work-up easier. No significant difference in yields was observed (see entries 4 and 5, Table 1).

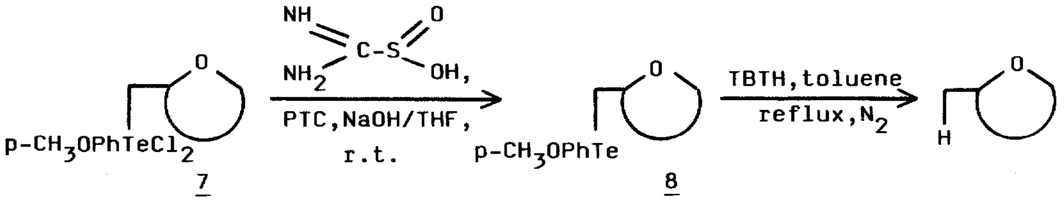
Capture of the intermediate free radical with methyl acrylate ocurred in good yield leading to 6. The reduced lactone (5) was obtained as a minor product (Eq. 3)[8].



(3)

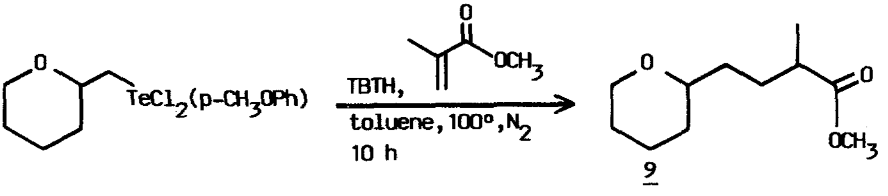
	5	6
a. *n* = 1	14%	72%
n = 2	18%	64%

Recently we reported that unsaturated alcohols are efficiently cyclized by reacting with aryltellurium trichlorides.[9] The aryldichlorotelluro ethers (7) were reduced in high yield to the corresponding tellurides (8) with thiourea dioxide in alkaline medium. In this work we found that both 7 and 8 can be detellurated by reacting with TBTH as described for the reduction of tellurolactones (1) and (2) (Eq. 4, Table 1)[7].



(4)

Capture of the intermediate free radical with methylmethacrylate led to the alkylated product (9)[8]. The reduced ether was not isolated owing to its volatility (Eq.5).



(5)

The results reported in this communication make aryltellurium trichlorides attractive reagents for cyclofunctionalization reactions. The reductive alkylation developed by us is to be compared with the ones reported elsewhere[10].

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References and Notes

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6. Unpublished results from our laboratory.
7. Reduction of tellurium-carbon bonds with tri-n-butyltin hydride - Typical procedure.
   To a solution of the dichlorotellurolactone (or ether) (1 mmol) in deoxygenated toluene (10 ml) under reflux and nitrogen atmosphere was added dropwise TBTH (4 mmol). The reaction was monitored by TLC. After the time indicated in Table 1 the solvent was evaporated and the residue was chromatographed on silica gel, eluting first with petroleum ether to remove tellurium and tin by-products, and then with petroleum ether/ethyl acetate (1:5) to give the tellurium free lactone or ether.
8. Reductive alkylation of tellurolactones and ethers - Typical procedure
   To a three necked flask (25 ml) containing the tellurolactone (or ether) (1 mmol) in deoxygenated toluene (2.5 ml) and methyl acrylate or methacrylate (1 ml) under reflux and nitrogen atmosphere was added TBTH (2 mmol) via a syringe pump for a period of 10 h. Then the solvent was evaporated and the residue was purified by column chromatography on silica gel, eluting first with petroleum ether to remove tellurium and tin by-products, and then with petroleum ether/ethyl acetate (1:5).
9. J.V. Comasseto, H.M.C. Ferraz, N. Petragnani and C.A. Brandt, Tetrahedron Lett., 28, 5611 (1987).
10. [a]Y. Araki, T. Endo, M. Tanji, Y. Arai and Y. Ishido, Tetrahedron Lett., 29, 2335 (1988); [b]W.P. Neumann, Synthesis, 665 (1987); [c]D.P. Curran, Synthesis, 417 (1988).

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