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Cyclization of Olefinic Benzyl Ethers with Aryltellurium Trichlorides

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SYNTHETIC COMMUNICATIONS, 22(6), 949-954 (1992)

CYCLIZATION OF OLEFINIC BENZYL ETHERS WITH ARYLTELLURIUM TRICHLORIDES

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Abstract: Olefinic benzyl ethers react with aryltellurium trichlorides leading to tetrahydrofurans in high yields. The reaction times and yields are similar to the analogous cyclization of the corresponding olefinic alcohols. The stereoselectivity of the transformation is low.

The cyclofunctionalization of double bonds by means of an electrophile is a very useful synthetic methodology[1]. Although the seleno- and the tellurocyclofunctionalization reaction were reported for the first time in the same paper[2] and the first cyclization procedure is nowadays a widely used synthetic transformation[3], the potentialities of the second were until recently not explored. Some time ago we[4,5] and others[6-9] demonstrated that tellurium oxide/lithium chloride in acetic acid[6,7], aryltellurinic anhydrides[8,9] and aryltellurium trichlorides[4,5] are efficient cyclization agents for olefinic carboxylic acids[4], alcohols[5-8] and carbamates[9]. Serious drawbacks to these methodologies were either the use of acidic conditions to perform the cyclization or the formation of hydrochloric acid during the reaction. In this communication we report that the cyclization of olefinic benzyl ethers promoted by aryltellurium trichlorides occurs under neutral conditions in high yield and at reaction times close to those observed for the cyclization of the corresponding alcohols (Eq.1, Table 1).

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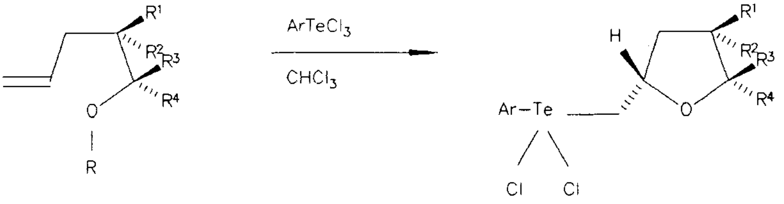


(Eq.1)

R = H, $CH_2C_6H_5$; Ar = p-$CH_3OC_6H_4$, p-$C_6H_4OC_6H_4$

TABLE 1 - Cyclization of Unsaturated Alcohols and Benzylethers with Aryltellurium Trichlorides

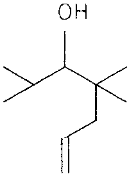
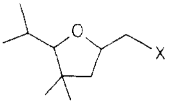
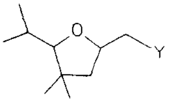
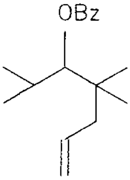
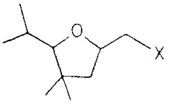
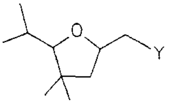
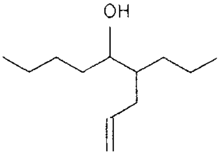
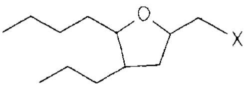
Alcohol/Benzyl Ether	Tetrahydrofuran	Reaction Time(h)	Reaction Temperature	Yield (%)*
1. 	a. 	0,25	reflux	98
	b. 	0,10	r.t.	97
2. 	a. 	0,30	reflux	97
	b. 	0,30	r.t.	97
3. 		0,33	reflux	85

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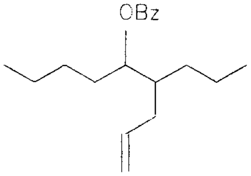
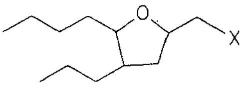
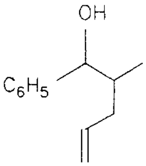
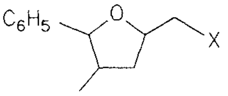
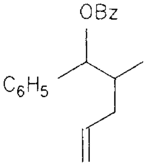
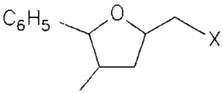
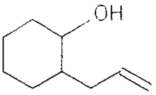
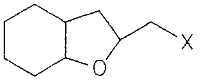
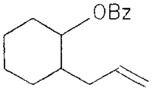
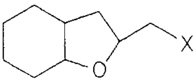
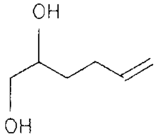
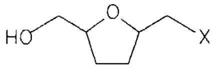
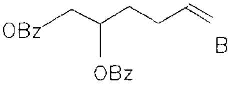
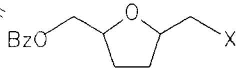
Table 1 Continued

4.			0,42	reflux	82
5.			0,50	reflux	88
6.			0,50	reflux	86
7.			0,25	reflux	90
8.			0,25	reflux	85
9.			0,7	reflux	96
10.			6,0	reflux	65

$X = p\text{-}CH_3OC_6H_4TeCl_2$; $Y = p\text{-}C_6H_4OC_6H_4TeCl_2$

*The analytical data for the compounds prepared agree with the proposed structures.

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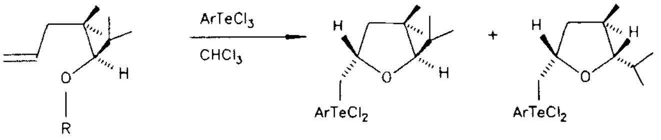
TABLE 2



R	Ar	Reaction Temperature(^{0}C)	cis/trans Ratio	Yield (%)	Reaction Time(min)
1. H	p-$CH_3OC_6H_4$	80	3:5	98	15
2. $C_6H_5CH_2$	p-$CH_3OC_6H_4$	80	1:1	97	18
3. H	p-$CH_3OC_6H_4$	80	2:3	96	30*
4. H	p-$C_6H_4OC_6H_4$	r.t.	2:3	97	5
5. $C_6H_5CH_2$	p-$C_6H_4OC_6H_4$	r.t.	2:3	97	30
6. H	p-$C_6H_4OC_6H_4$	0	1:2	98	120

*Although the reaction was instantaneous, the mixture was maintained under reflux for 30 min to verify if some change in the isomer ratio occurred.

In Table 2 is shown that the reaction times for a particular unsaturated alcohol and the corresponding benzyl ether with p-methoxyphenyltellurium trichloride at 80^{0}C are practically the same. The reaction of the alcohol 1 (Table 1) with p-phenoxyphenyltellurium trichloride is exothermic leading to the cyclic ether in 97% yield after 5 minutes. The same reaction can be performed at 0^{0}, but requires a reasonably longer reaction time (Table 2). The reaction of the corresponding benzyl ether at room temperature leds to the same product after 30 minutes.

Concerning the stereocontrol of the reaction it was found that the selectivity is low for the substrates and nucleophiles studied. The cyclization of 2,4,4-trimethyl-hept-6-en-3-ol and the corresponding benzyl ether was studied in more detail (Table 2). When the substrate was the alcohol the **trans** isomer

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predominated under all reaction conditions employed (entries 1, 3, 4, 6; Table 2). In one case (entry 2; Table 2) the cyclization of the benzyl ether was non-selective, giving a 1:1 mixture of the **cis** and the **trans** products, the selectivity for the **cis** isomer being however enhanced relative to the reaction with the corresponding alcohol (entry 1; Table 2). As the stereoselectivity of the cyclofunctionalization reactions is the result of a balance between electronic and steric factors, other protecting groups for the alcohol and other tellurium electrophiles are being tested attempting to improve the stereoselectivity.

The unsaturated alcohols used in this study were prepared by alkylation of the appropriate ketone enolate with allyl bromide[10] followed by reduction with sodium borohydride[11]. Alcohol **9** (Table 1) was commercially available and alcohol **7** was prepared by reaction of cyclohexene oxide with allylmagnesium bromide[12]. The benzyl ethers were prepared by reacting the appropriate alcohol with sodium hydride followed by alkylation with benzyl chloride[13]. The aryltellurium trichlorides were prepared by reacting tellurium tetrachloride with the corresponding aromatic ether[14].

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15. **Typical Procedure for the Cyclization of Unsaturated Alcohols with p-Phenoxyphenyltellurium Trichloride**

To a solution of the unsaturated alcohol (entry 1, Table 1; 0.156 g, 1 mmol) in anhydrous chloroform (15 ml), at room temperature was added p-phenoxyphenyltellurium trichloride (0.403 g, 1 mmol). An exothermic reaction occurred. After 5 min of stirring the reaction mixture turned limpid; then the solvent was evaporated in a rotatory evaporator and the residue was recrystallized from chloroform/petroleum ether: 0.50g (97%); m.p.: 108-110°C; I.R. (KBr): 1243; 1485; 1576; ^{1}HNMR ($CDCl_3$/TMS, δ): 0.85-1.26(m,6H); 1.48-2.11(m,3H); [3.14(d,J 8.5); 3.37(d,J 7.32)1H]; [3.86(d,J 7.4); 3.95 (d,J 7.32)2H]; 4.59-4.79(m,1H); 6.95-7.39(m,7H); 8.03(d,J 8.79, 2H); Anal. calcd. for $C_{22}H_{28}Cl_2O_2Te$: C, 50.52; H, 5.39. Found: C, 50.47; H, 5.05.

16. **Typical Procedure for the Cyclization of Unsaturated Benzyl Ethers with p-Phenoxyphenyltellurium Trichloride**

A mixture of the benzyl ether (entry 2, Table 1; 0.246 g, 1 mmol) and p-phenoxyphenyltellurium trichloride (0.403 g, 1 mmol) in anhydrous chloroform (15 ml) was stirred for 30 min at room temperature, then the solvent was evaporated and the residue was filtered through a column of silica gel eluting with chloroform. Evaporation of the solvent in a rotatory evaporator followed by recrystallization of the residue from chloroform/petroleum ether and washing several times with petroleum ether gave 0.50 g (97%) of a product with identical physical characteristics of that obtained in the preceding experiment.

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