

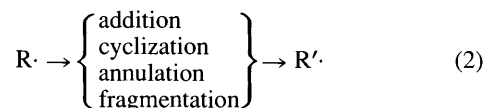
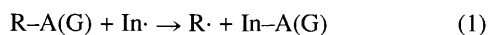
Novel Group Transfer Cyclization Reactions of Organotellurium Compounds

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When irradiated in the presence of hexabutyliditin, readily available *O*-allylated and *O*-prop-2-ynylated 2-hydroxyalkyl aryl tellurides undergo group transfer cyclization to afford 2,4-disubstituted tetrahydrofuran derivatives.

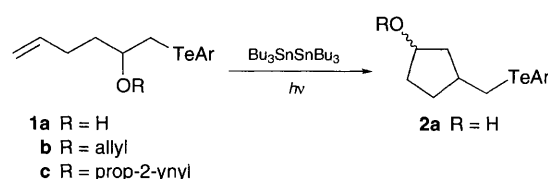
Interest in organic radical reactions has rapidly increased over the past several years as radical-based methods for organic synthesis have evolved.¹ In atom and group transfer-mediated radical reactions, [eqns. (1)–(3)], an atom A (hydrogen,²



halogen³ or metal⁴) or a group G (such as SePh⁵) is transferred in the chain-transfer step [eqn. (3)] from a neutral molecule to a radical R· to form a new σ-bond and a new radical. For such processes to be synthetically useful, the atom/group transfer step has to be preceded by a radical addition, cyclization, annulation or fragmentation reaction [eqn. (2)]. In 1988 Barton and coworkers reported efficient exchange of radicals *via* diorganyl tellurides.⁶ Thus, when alkyl aryl tellurides were allowed to react with methyl radicals, aryl methyl telluride and a carbon centred radical⁷ were formed. Recent *ab initio* calculations on Me₂HTe· suggest that the tricoordinate tellurium-centred radical involved in the exchange is an intermediate rather than a transition state.⁸ The scarce rate data on PhTe group transfer also suggest rapid transfer of PhTe groups to radicals [*k* is similar in eqn. (3) for A = I and G = PhTe⁹]. To the best of our knowledge, the photo-stimulated cyclization of unsaturated acyl tellurides¹⁰ and the AIBN-induced addition of diorganyl tellurides of acetylenes¹¹ are the only examples of group transfer reactions of organotellurium compounds. We demonstrate in the present paper that these types of reactions are of much wider scope in organic synthesis.

Due to the ready cyclization of the hex-5-enyl radical, 2-hydroxyhex-5-enyl aryl tellurides **1a** were initially con-

sidered as suitable substrates for group transfer reactions. These compounds were prepared in high yields (70–90%) by regioselective ring-opening of 1,2-epoxyhex-5-ene with arenetellurolate ions (generated by sodium borohydride reduction of the corresponding ditellurides). When 0.05 mol dm⁻³ solutions of compounds **1a** in refluxing benzene, containing 40 mol% of hexabutyliditin, were irradiated under nitrogen with a sun lamp, the starting materials were consumed within 2–6 h, and cyclopentane derivatives **2a** were isolated in fair yields after column chromatography as *cis/trans*† mixtures (Scheme 1; Table 1). Among the different aryl groups tested, the 4-trifluoromethylphenyl group turned out to be superior with respect to the time required to obtain complete conversion and also with respect to the stability of the organotellurium intermediates and products. The isolated yields and isomeric compositions did not differ much, though. The β-hydroxyalkyl aryl tellurides were readily *O*-allylated in dry tetrahydrofuran on treatment with allyl bromide and sodium hydride. When the allylated compound **1b** (Ar = Ph) was submitted to the usual group transfer cyclization conditions, cyclization occurred in the 5-*exo* mode to form exclusively (> 95%) the tetrahydrofuran derivative **3** as a *cis/trans* mixture. This is not unexpected in view of the strongly activating effect of a 3-oxa substituent in hex-5-enyl radical cyclizations.¹ Similarly, *O*-prop-2-ynylated compound **1c** (Ar = 4-trifluoromethylphenyl) afforded the vinylic telluride **4** as an *E/Z*-mixture.‡ Due to difficulties in the attempted purifications of the *O*-prop-2-ynylated products the following group



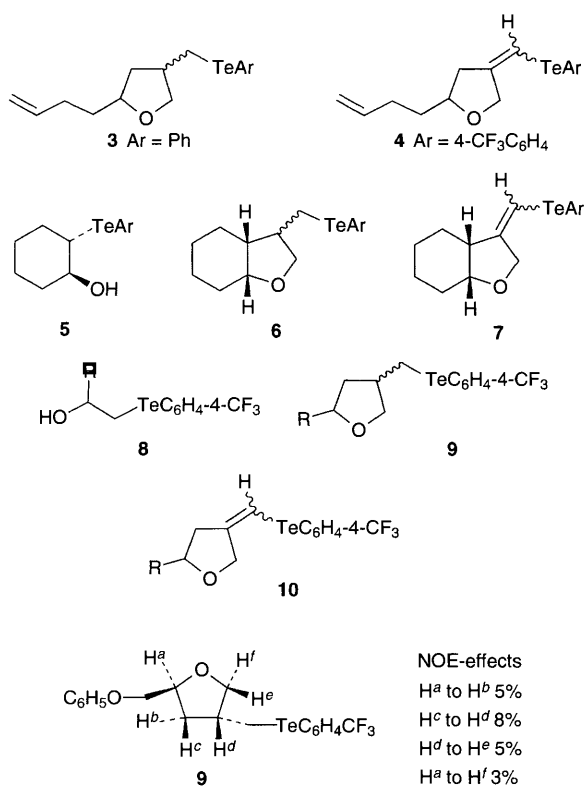
Scheme 1

Table 1 Group transfer cyclization reactions of organotellurium compounds

2-Hydroxyalkyl aryl telluride	<i>O</i> -Allylation yield (%)	<i>O</i> -Prop-2-ynylation yield (%) ^a	Group transfer product ^b (% yield; <i>cis/trans</i> -ratio ^d)	Group transfer product ^c (% yield; <i>E/Z</i> -ratio ^e)
1a Ar = Ph	—	—	2a (68; 1.3 : 1)	—
1a Ar = C ₆ H ₄ -4-NMe ₂	—	—	2a (63; 1.3 : 1 ^f)	—
1a Ar = C ₆ H ₄ -4-CF ₃	—	—	2a (73; 1.3 : 1 ^f)	—
1a Ar = 2-thienyl	—	—	2a (75; 1 : 1)	—
1a Ar = Ph	56	(47)	3 (60; 1 : 4 ^g)	4 (40; 1.3 : 1)
1a Ar = 2-thienyl	nd	—	3 (63; 1 : 4 ^g)	—
1a Ar = C ₆ H ₄ -4-CF ₃	—	(70)	—	4 (46; 1.5 : 1)
5 Ar = C ₆ H ₄ -4-CF ₃	80	(55)	6 (69; 2 : 1)	7 (40; 1.2 : 1)
5 Ar = 2-thienyl	60	—	6 (72; 2 : 1)	—
8 R = Et	63	(37)	9 (64; 1 : 3)	10 (49; 1 : 1.2)
8 R = Ph	75	(47)	9 (65; 1 : 3)	10 (47; 1 : 1.2)
8 R = CH ₂ O-allyl	73	82 (51)	9 (54; 1 : 10)	10 (47; 1 : 1)
8 R = CH ₂ OPh	81	95 (31)	9 (64; 1 : 4)	10 (48; 1 : 1.1)
8 R = CH ₂ OBz	74	80 (36)	9 (60; < 1 : 20)	10 (46; 1 : 1.1)

^a Values in parentheses are isolated yields after flash chromatography. ^b Except for compounds **2a**, these compounds were obtained from *O*-allylated 2-hydroxyalkyl aryl tellurides. ^c These compounds were obtained from *O*-prop-2-ynylated 2-hydroxyalkyl aryl tellurides. ^d As determined by NOESY and NOE experiments. For compounds **6** the *exo/endo* ratio is given. ^e As determined by NOE experiments. ^f The isomeric ratio was obtained from the ¹H NMR spectrum of the mixture in analogy with the results for compound **2a** (Ar = Ph). ^g Due to overlapping signals in all solvents tried, the assignment of isomers could not be performed. The *trans* isomer is believed to predominate.

transfer cyclization step was sometimes effected using the crude product (see Table 1). However, this could be effected only in modest yields. Cyclohexene oxide was ring-opened (compound **5**), allylated/prop-2-ynylated and group transfer cyclized to give *cis*-fused compounds **6** and **7**, respectively. The *exo* configuration of compound **6** predominated (2 : 1) as determined by NMR experiments on the hydrodetellurated ($\text{Bu}_3\text{SnH-AIBN}$) compound.[‡] The terminal epoxides 1,2-epoxybutane, styrene oxide, allyl glycidyl ether, glycidyl phenyl ether and glycidyl benzyl ether were all ring-opened by sodium 4-trifluoromethylphenyltelluroate (compounds **8**), allylated/prop-2-ynylated and group transfer cyclized to give tetrahydrofuran derivatives **9** and **10**, respectively. As can be seen in Table 1, the *trans* isomer of compounds **9** is always the predominating product. However, when R contains an oxygen at position 2, this isomer is almost exclusively formed.[‡] We hypothesize that this is due to chelation of the extra oxygen to the tricoordinate tellurium-centred radical intermediate, favouring a transition state where the 2- and 4-substituents are oriented *trans* to each other. In view of the ready manipulation of organotellurium compounds (*e.g.* via telluroxide elimination or cuprate reactions¹⁰) we feel that the methodology presented herein would be useful for the regiocontrolled construction of more complex tetrahydrofuran derivatives.



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Footnotes

[†] The stereochemistry was determined after benzylation, hydrodetelluration ($\text{Bu}_3\text{SnH-AIBN}$) and comparison with an authentic sample obtained by benzylation of commercially available 3-methylcyclopentanol. By DEPT, INEPT, NOESY, PECOSY, HSQC, NOE and ZTOCSY experiments it was possible to assign the *cis* isomer of 3-methylcyclopentanol benzoate as the one with the methyl resonance shifted towards lower field.

[‡] The assignment of *cis/trans*, *E/Z* and *exo/endo* isomers were based on NOESY and NOE-diff. experiments as demonstrated below for compound **9** (R = CH₂OPh).

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