1,4-Fragmentation of γ-Tributylstannyl Alcohols by a Hypervalent Organoiodine Compound: a New Synthesis of Unsaturated Carbonyl Compounds

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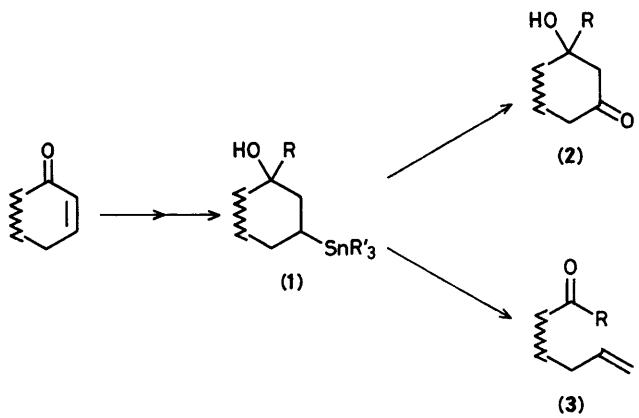
1,4-Fragmentation of γ-tributylstannyl alcohols using iodosylbenzene, boron trifluoride–diethyl ether, and dicyclohexylcarbodiimide produces unsaturated carbonyl compounds; the fragmentation, combined with conjugate addition of tributylstannyl-lithium and reduction or alkylation, offers an efficient procedure for the reductive and alkylative ring opening of cyclic vinyl ketones.

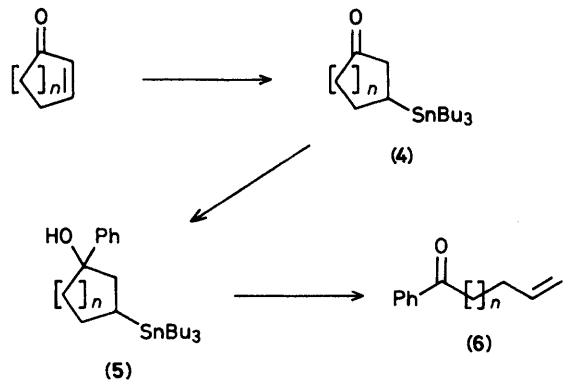
Stannyl alcohols have been shown to be important intermediates in organic synthesis. 1,3-Eliminative cyclization of acyclic γ-stannyl alcohols and their derivatives by reaction with thionyl chloride, triphenylphosphine dibromide, or boron trifluoride–diethyl ether proved to be useful for the synthesis of substituted cyclopropane derivatives.[1] Chromic anhydride oxidation of the cyclic γ-stannyl alcohol (**1**) has been reported to produce the γ-hydroxy ketone (**2**), as shown in Scheme 1, and the reaction was utilized as a key step in alkylative enone transposition.[2] The reaction mode, however, was found to be completely altered if a hypervalent organoiodine compound was used as the oxidizing agent. We now report a new oxidative 1,4-fragmentation[3] of the cyclic γ-stannyl alcohol (**1**) to produce the unsaturated carbonyl compound (**3**).



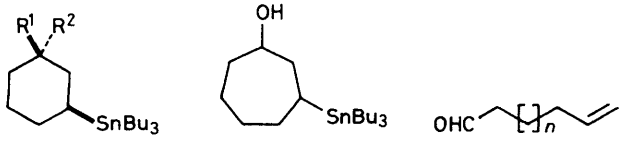
Scheme 1

The required organotin compounds (**5**) containing a tertiary hydroxy group were prepared in a straightforward fashion from unsaturated cyclic ketones:[2] 3-tributylstannylcyclopentanone (**4a**), prepared from cyclopent-2-en-1-one by conjugate addition of tributylstannyl-lithium in tetrahydrofuran (THF),[2,4] on treatment with phenyl-lithium (2 equiv.) in THF, afforded the tertiary alcohol (**5a**) as a stereoisomeric mixture (46:54) in 58% yield. Similarly, the alcohols (**5b**) and (**5c**) were prepared by phenylation of the ketones (**4b**) and (**4c**) in 78 and 76% yields, respectively.

We have reported that the reactivity of iodosylbenzene toward nucleophiles can be considerably enhanced by the co-ordination of Lewis acids to the oxygen atom.[5] When the γ-stannyl alcohol (**5b**) was treated with iodosylbenzene and



Scheme 2. **a**; $n = 1$ **b**; $n = 2$ **c**; $n = 3$



(7) a; R^1 = OH, R^2 = H
b; R^1 = H, R^2 = OH

(8)

(9) a; n = 1
b; n = 2

Table 1. 1,4-Fragmentation of γ-stannyl alcohols.

Alcohol	Reaction time/h	Product	Yield[a]/%
(**5a**)	5	(**6a**)	(63)
(**5b**)	4	(**6b**)	81
(**5c**)	2.5	(**6c**)	86
(**7a**)	2	(**9a**)	(74)
(**7b**)	3	(**9a**)	(74)
(**8**)	3	(**9b**)	(55)

[a] Isolated yield. G.l.c. yields are shown in parentheses.

boron trifluoride–diethyl ether at 0 °C, t.l.c. showed that (**5b**) had completely disappeared, but the unsaturated ketone (**6b**) was not obtained. Use of dicyclohexylcarbodiimide (DCC) was found to be essential for the 1,4-fragmentation of (**5b**): a solution of boron trifluoride–diethyl ether and DCC in dichloromethane, which had been stirred for 1 h at room temperature, was added to a mixture of (**5b**) and iodosylbenzene at 0 °C under nitrogen. After stirring for 4 h at room temperature, the ring-opening product (**6b**) was isolated by preparative t.l.c. in 81% yield. Fragmentation of the 5- and 7-membered cyclic alcohols (**5a**) and (**5c**) also proceeded smoothly to give the corresponding unsaturated ketones.

We have found that the fragmentation might also be effective for the synthesis of the unstable enals (**9**). $NaBH_4$ reduction of (**4b**) in methanol produced the *cis*- and *trans*-alcohols (**7a**) and (**7b**) in a ratio of 89 : 11 (92% yield). Their stereochemistry was determined by ^1H and ^{13}C n.m.r. spectroscopy.[6] Reduction of (**4c**) also afforded a mixture of stereoisomers of (**8**) (62 : 38) in 76% yield. 1,4-Fragmentation of either stereoisomer of (**7**) using iodosylbenzene, boron trifluoride–diethyl ether, and DCC in dichloromethane smoothly gave the same yield of the unstable hex-5-enal (**9a**). The results are summarized in Table 1.

The mechanism of the fragmentation is not yet clear but the reaction should be useful for the reductive and alkylative ring opening of unsaturated cyclic ketones.

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