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A HIGHLY REGIO- AND STEREOSELECTIVE SYNTHESIS OF INTERNAL OLEFINS VIA AN ELIMINATION OF TRIMETHYLSTANNYL GROUP

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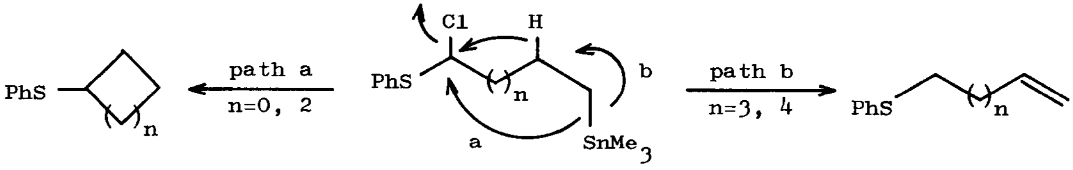
Abstract: Internal reaction of secondary alkyltin(IV) compounds having thionium ion gave internal trans olefins with high yield and regio- and stereoselectivity via 1,5- or 1,6-transfer of a hydride β to the trialkylstannyl group.

Some time ago, Macdonald and his group carried out the internal reaction of tetraalkylstannanes having carbon-centered electrophiles, and found two modes of reactions resulting either in the carbon-carbon bond formation to produce cyclization products or in the transfer of a hydride β to the trialkylstannyl group to produce terminal olefins.1) We then investigated the thionium ion-induced2) reaction of alkyltin(IV) compounds derived from 1 using titanium(IV) chloride, and found that cyclization (path a) predominated when n = 0 or 2, while β-hydride transfer (path b) predominated when n = 3 or 4.3) The finding that the reaction modes are strictly dependent on the alkyl chain



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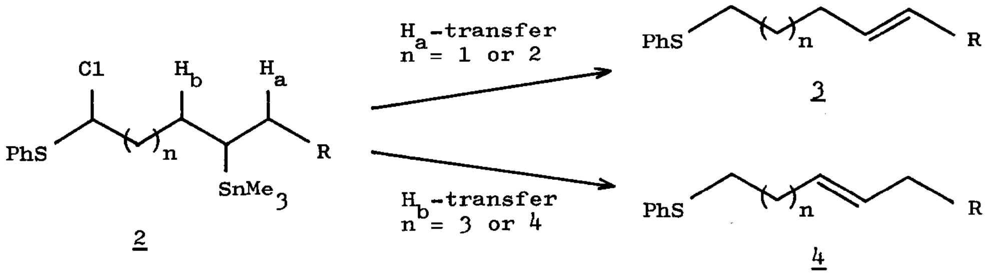
length prompted us to examine whether there exists a selectivity among H_a-, H_b-transfer or cyclization in the secondary alkyltin(IV) compounds 2 (Scheme I). Actually, a hydride transfer with excellent regioselectivity as well as stereoselectivity was observed, and the reaction turned out to be a useful synthetic method of internal olefins with trans geometry.



a R = Me, n = 1
b R = Me, n = 2
c R = Et, n = 2
d R = Me, n = 3
e R = Me, n = 4

Scheme I

Table I. Elimination of the Secondary Alkyltin(IV) Compound.[a]

Alkyltin(IV)	Temperature (°C)	Product	Yield[b] (%)	trans (%)	cis (%)
2a	-100	3a	-	100	0
	-78		95	98	2
	0		90	91	9
	rt		91	80	20
2b	0	3b	91	84	16
2c	0	3c	85	100	0
2d	-78	4d (= 3c)	93	99	1
2e	0	4e	96	90	10

a) Chlorides 2 were treated with 1 eq of titanium(IV) chloride in dichloromethane for 15 min.

b) Yields are based upon the sulfides before the chlorination.

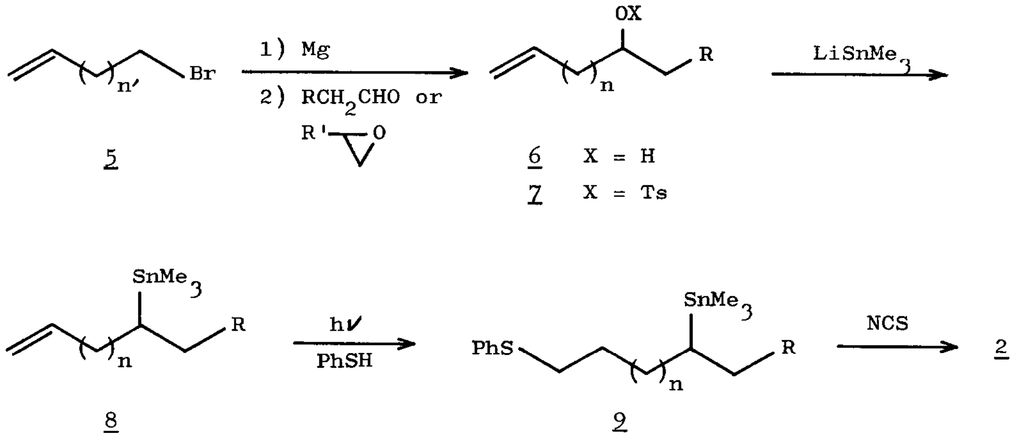
The secondary alkyltin(IV) compounds 2a, 2b, and 2c, upon treatment with 1 eq of titanium(IV) chloride, produced olefins 3a, 3b, and 3c, respectively, through H_a-transfer, while 2d and 2e produced corresponding olefins 4d and 4e through H_b-transfer. The results are summarized in the Table I. The trans structure was assigned for all of the major products in view of the strong IR absorption at 966 cm^{-1} and coupling constant of 15.2 Hz between two olefinic protons observed in the 400-MHz NMR spectra of the samples isolated on a preparative GLC. The cis isomers corresponding to 3a and 3b were prepared by the known routes, and used as references.

The characteristic features of the results are as follows. (1) Among the possible reaction modes, 2a and 2d underwent only 1,5-hydride transfer, while 2b, 2c, and 2e underwent only 1,6-hydride transfer. The selectivity was quite high and the products did not contain any trace of cyclization products nor position isomers of the double bond. (2) The better trans selectivity was observed at the lower temperature. (3) Although 1,5-hydride transfer proceeded smoothly at -78°C, the 1,6-hydride transfer required the higher reaction temperature, inevitably with the lower stereoselectivity. (4) The trans stereoselectivity in the 1,6-hydride transfer, however, was improved when the alkyl group on the β-position of the stannyl group became bulkier (2b vs. 2c).

The absence of the cyclized products would indicate that the cyclization process in the present case is unfavorable due to the substantial steric interaction at the secondary carbanion center bound to the stannyl group.

Extremely facile processes of 1,5- and 1,6-hydride transfer might be responsible for the high regioselectivity in the present reaction. The high stereoselectivity could be explained by assuming a cyclic intermediate of thermodynamically stable conformation, in which the trimethylstannyl group and the migrating hydrogen atom occupy the anti-coplanar position.

The secondary alkyltin(IV) compounds 2a - 2e were prepared from ω-bromo-1-alkenes 5 as shown in the Scheme II. The Grignard compounds from the bromides 5 were treated with appropriate aldehydes or epoxides to give secondary alcohols 6 in 49 - 82% yields. The tosylates 7 derived from 6 (76 - 91%) were converted to alkyltin(IV) compounds 8 by treatment with trimethylstannyllithium in THF.[4] UV-Irradiation of the crude oil 8 in thiophenol gave sulfides 9,



Scheme II

accompanied by diphenyl disulfide. The byproduct was removed after reducing it to thiophenol by treating the mixture with lithium aluminum hydride or triphenylphosphine. The overall yields of 9 from 7 were 48 - 51%. Treatment of the sulfides 9 with N-chlorosuccinimide in carbon tetrachloride gave α-chlorinated sulfides 2 in quantitative yield as an almost pure oil after the filtration of succinimide.

The present reaction offers a valuable approach for the introduction of an internal trans double bond into an organic molecule regio- and stereoselectively.

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