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Preliminary communication

HYDROGEN TRANSFER FROM CROTYLTRI-n-BUTYLSTANNANE TO CARBON RADICALS

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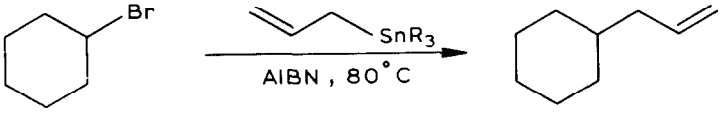
Summary

Attempted reaction of carbon centered radicals with crotyltri-n-butylstannane leads not to C—C bond formation as with 2-propenyltri-n-butylstannane, but to hydrogen abstraction resulting in production of butadiene and tri-n-butylstannyl radicals.

Recently we reported [1] upon a free radical chain process for C—C bond formation which proved remarkably successful with highly functionalized organic substrates, in particular those sensitive to reductive elimination reactions, as summarized in equation 1 below for the simple case of conversion of bromocyclohexane to allylcyclohexane. The purpose of our present discussion is to disclose a serious competing side reaction which occurs upon alkyl substitution of 2-propenyltri-n-butylstannane in the 3 position of the propenyl unit. As a result, stannanes such as 2-butenyltri-n-butylstannane are ineffective reagents for utilization in such "allyl transfer" reactions [2].



(1)

For the present study, we selected substrates which had been previously shown to undergo smooth, reproducible, and high yield reactions with 2-propenyltri-n-butylstannane [1] (hereafter referred to as allyltri-n-butylstannane, 1) and studied their reaction with 2-butenyltri-n-butylstannane [3] (hereafter referred to as crotyltri-n-butylstannane, 2). Precursors to carbon centered radicals were allowed to react with this reagent using various initiation methods and temperatures and the products produced were isolated by column chromatog-

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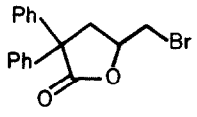
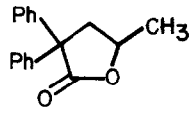
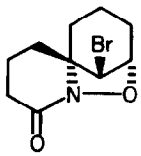
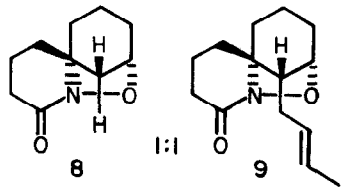
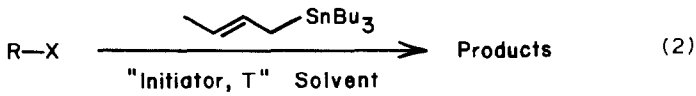
TABLE 1 [a]

Run	Substrate	Stannane	Conditions (yield)	Product
1	 3	2	A (0)	 4
2		2	B (78)	
3		2	C (70)	
4		2	D (0)	
5	1-Bromodecane 5	2	A (0)	n-Decane 6
6		2	C (52)	
7	 7	2	A (0)	 8 1:1 9
8		10	A (66)	

[a] (A) toluene, 80°C, AIBN, 8 h; (B) xylene, reflux, di-t-butylperoxide, 8 h; (C) chlorobenzene, reflux, di-t-butylperoxide, 8 h; (D) toluene, $h\nu$, 25°C, 2 h [10].

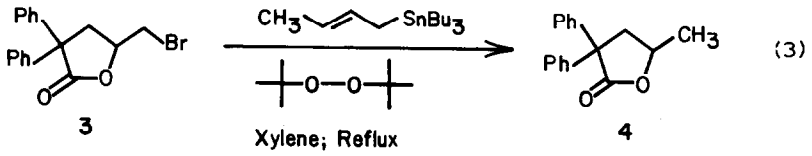
raphy, and/or analyzed by gas chromatography. Structures were determined by routine spectroscopic methods and compared with authentic or independently synthesized samples. Note equation 2 below. Products (and chemical yields) are given in Table 1.



(2)

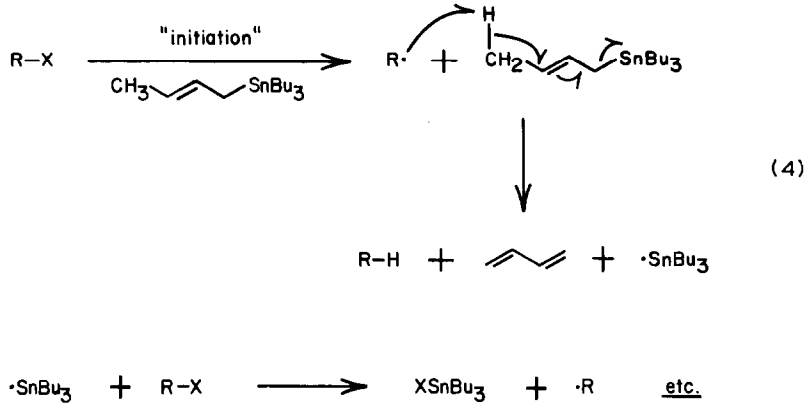
Not surprisingly [4], this stannane was found to be less reactive than allyltri-n-butylstannane towards carbon centered radicals. In general, chemically initiated reactions at 80°C in toluene failed to lead to detectable [5] levels of product formation (TLC, NMR, VPC) even though conditions duplicated those utilized successfully previously with allyltri-n-butylstannane. The photochemical protocol [1] ($\lambda > 300$ nm, ambient) was similarly unsuccessful.

Consumption of starting materials was observed, however, under more forcing conditions. For example, lactone 3 was allowed to react with crotyltri-n-butylstannane (2) (2.0 eq.) in refluxing xylene (initial substrate concentration 0.5 *M*) with di-t-butylperoxide as initiator [6]. After 8 h, complete consumption of starting material (TLC [7] R_f 0.15 in 10% THF/hexanes) was noted with production of a faster running product (TLC R_f 0.21 in 10% THF/hexanes). Isolation by column chromatography afforded the reduced product 4 in 78% isolated yield. Note equation 3.



(3)

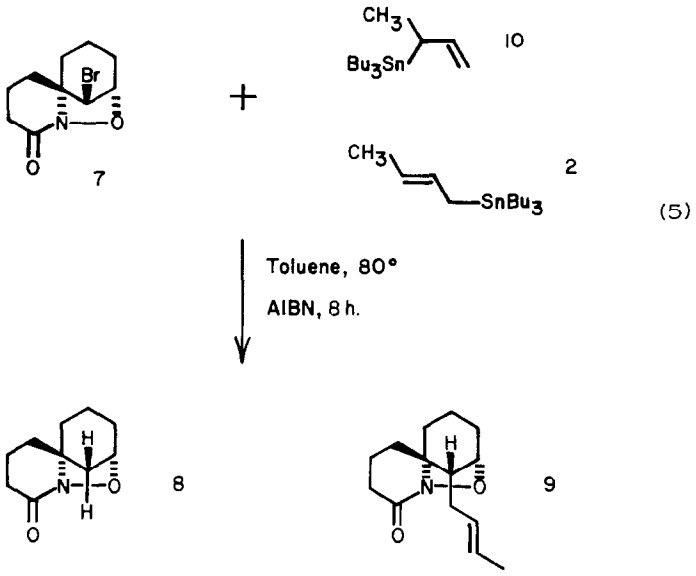
Initially, we were unsure as to the origin of the new hydrogen atom in 4 since xylene, a potential hydrogen donor, was employed as solvent. However, the same result was observed utilizing non-hydrogen donating solvents (e.g. chlorobenzene) with 3 and other substrates (Table 1, vide infra), and, moreover, xylene and toluene were successfully utilized as solvents with allyltri-n-butylstannane. Thus it would appear that crotyltri-n-butylstannane is the source of hydrogen which leads to 4 [8]. Mechanistic reasoning (note equation 4 below) would suggest that butadiene should be produced in such reactions. This expectation was easily verified by trapping butadiene with bromine after completion of reaction (run 6, Table 1) [9].



(4)

In one case, we attempted to utilize a mixture [2] of crotyltri-n-butylstannane (**2**) and 3-(tri-n-butylstannyl)-1-butene (**10**) to effect "allyl transfer" from the presumably more reactive isomer **10** (note equation 4), even though this material is known [3] to undergo facile isomerization to its more stable cogener **2**. In the event, a ca. 6/4 mixture of **2** and **10**, produced by reaction of Bu_3SnCl with the Grignard reagent prepared from 3-chloro-1-butene, was reacted with substrate **7** (note run 8, Table 1) at 80°C in toluene. It should be noted that, due to the preponderance of the undesired stannane in the mixture utilized, a ca. 10 fold excess of stannane was employed. The desired allyl transfer product, **9**, was obtained along with reduced product **8** in a ratio of ca. 1/1. (Note equation 5)

Since **7** is unreactive with crotyltri-n-butylstannane (**2**) under the conditions utilized in this case (note run 7 above), it would appear that **10** is an even more powerful hydrogen donor than **2**. Given the difficulty of preparing **10** uncontaminated with **2**, we are not able to verify this point. However, only the parent allyltri-n-butylstannane or derivatives with alkyl substitution in the 2 position of the



allyl unit have to date been used without complication in the allyl transfer reaction. Investigations on the scope of such reactions as a function of structure in the organostannane partner are the subject of ongoing investigations in our laboratories.

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References and Notes

1 G.E. Keck and J.B. Yates, J. Am. Chem. Soc., 104 (1982) 5829.
2 Our observations are in contrast to those of Grignon and Pereyre. Note: J. Grignon and M. Pereyre, J. Organomet. Chem., 61 (1973) C33.
3 This material was prepared by the procedure of E. Matarasso-Tchiroukhine and P. Cadiot, J. Organomet. Chem., 121 (1976) 169. Care was taken to insure complete isomerization of the mixture of butenylstannanes so obtained to the more stable 2-butenyl isomer prior to use in the reactions described herein.
4 Based on known substituent effects on various free radical processes, a decrease in rate of ca. 10—50 fold would be expected for reaction of **2** (as compared to **10**) according to the mechanism suggested in ref. 1. Note Walling, Cheves, Free Radicals in Solution, John Wiley and Sons Inc., 1957, p. 121 and 131.
5 Since authentic samples of the reduced products obtained under more forcing conditions were in hand, as were analytical chromatographic methods for their analysis, as little as 5% conversion would have been readily detected.
6 Di-t-butyl peroxide was chosen so as to provide a reasonable initiator lifetime at the reaction temperature employed. For the halflives of commonly used initiators as a function of temperature, note Walling, Cheves, Free Radicals in Solution, John Wiley and Sons, Inc., 1957, p. 469.
7 All thin layer chromatographic analyses (TLC) were performed on Merck 0.25 mm glass plates. Visualization of developed plates was via fluorescence quenching and staining with phosphomolybdic acid.

8 One possible explanation for this reduction process would be contamination of the crotyltri-n-butylstannane by tri-n-butyltin hydride. However, we were unable to detect tri-n-butyltin hydride in our sample by either IR spectroscopy or VPC analysis. In addition, subjecting crotyltri-n-butylstannane to the reaction conditions in the absence of substrate did not result in formation of tri-n-butyltin hydride, as determined by VPC and IR analysis.

9 The trapping experiment was performed as follows. Run 6 of Table 1 was performed in a sealed pyrex tube, which was cooled to -78°C before opening at the completion of reaction. Cold methylene chloride was added, followed by excess bromine, and the mixture was allowed to warm to room temperature. VPC analysis showed peaks identified by retention time as *trans*-1,4-dibromo-2-butene and 1,2,3,4-tetrabromobutane (by comparison with authentic samples), whose structures were confirmed by GC-MS analysis. As the amounts of these materials produced was much lower than theory (most probably due to consumption of butadiene by polymerization processes under the reaction conditions) we were unable to obtain any quantitative data on the amount of butadiene actually produced during the reaction.

10 Photochemical initiation (method D) was achieved by using a conventional 450-W Hanovia medium-pressure mercury lamp equipped with a Pyrex filter.