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Stereoselective Conversion Of Tetraalkyltin Compounds to Alcohols

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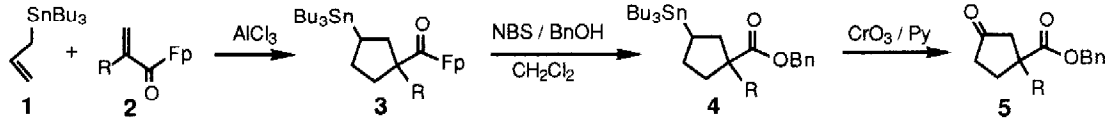
Summary: A stereoselective method for the conversion of a tributyltin group at an unactivated carbon atom has been achieved. Reaction with bromine leads to preferential cleavage of a butyl group, giving an alkylbromodibutylstannane. Subsequent reaction with basic peroxide leads to preferential cleavage of the more-substituted carbon-tin bond and formation of the corresponding alcohol with retention of configuration.

Organotin reagents have emerged as valuable reagents for synthetic organic chemistry[1]. In certain types of organotin compounds, most notably allylstannanes and vinylstannanes, the relative ease of cleavage of the carbon-tin bond has made these reagents particularly valuable as compounds which can transfer these groups. Unless an activating substituent such as a alkene is in the vicinity, the carbon-tin bond is relatively difficult to cleave. Further complicating this problem is the tetravalent nature of tin, and in addition to the organic substituent of interest, one must also be concerned with competing processes that might happen at the other alkyl groups at tin. Successful cleavage reactions of tetraalkylstannanes have been realized mostly through intramolecular reactions of carbocations, which form three-[2] and/or five-membered rings[3]. As part of a related project[4], we sought to develop a method for the stereoselective cleavage of tetraalkyltin compounds. Reaction of α,β-unsaturated acyliron complexes with allylstannanes leads to the formation of cyclopentane derivatives such as **3** (Scheme 1). Reaction of these complexes with N-bromosuccinimide in the presence of alcohols leads to the ester derivatives in good yield. Cleavage of the tetraalkyltin substituent is easily accomplished using chromium trioxide-pyridine, giving the ketone derivative **5**. We sought a method for cleavage of the tributyltin substituent which would leave the stereochemistry intact. Such a method

Scheme 1



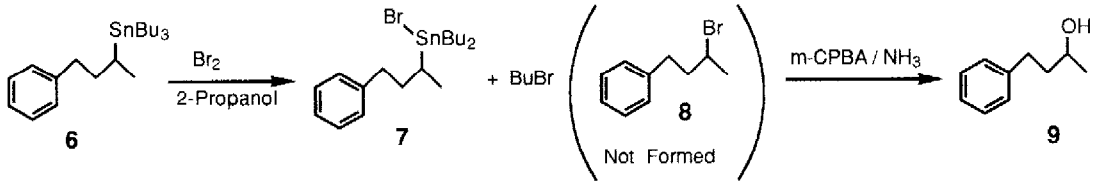
1 **2** **3** **4** **5**

Fp = -Fe(C_5H_5)(CO)$_2$; Bn = CH_2Ph
A. R = H; B. R = CH_3

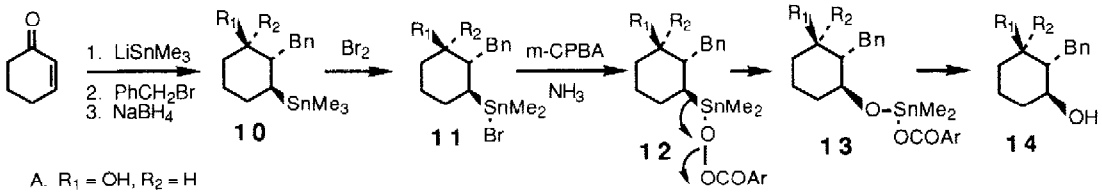
would make the overall [3+2] cycloaddition reaction more attractive from a synthetic standpoint. Also, the simpler derivatives might be more amenable to accurate stereochemical assignments. In our original communication, we suggested that the relative stereochemistry of the acyliron and tributyltin substituents was cis based on ^{13}C - ^{119}Sn coupling constants. A crystalline derivative suitable for X-ray analysis containing the tributyltin or trimethyltin moieties could not be found.

Although selective cleavage of unactivated tetraalkyltin compounds has not been reported, some success has been realized with tetraalkylsilanes[5]. In cleavage of tetraalkyltin compounds with electrophiles, the relative order for cleavage of alkyl groups is known to be methyl > primary > secondary > tertiary[6]. In addition, in a compound such as **6** statistics also favor cleavage of a butyl group over the single secondary alkyl group. Reaction of compound **6** with bromine in 2-propanol according to the procedure of Gielen[6] led to clean butyl cleavage, giving bromostannane **7** with no detectable amount of bromide **8**. Treatment of **7** with basic m-CPBA led to formation of the alcohol **9** in 86% overall yield from stannane **6** (Scheme 2)[7].

Scheme 2



Scheme 3

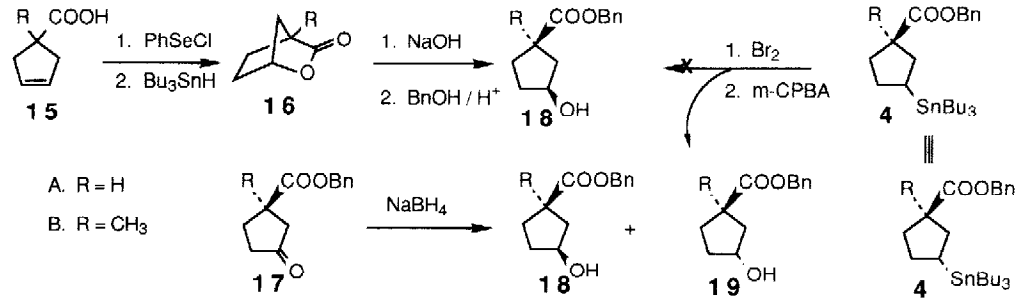


In the next phase of these studies, the stereoselectivity of the cleavage reaction was examined. Stannyl alcohols **10A** and **B** were synthesized from 2-cyclohexenone according to the sequence of reactions in Scheme 3. Cleavage of alcohol **10A** with bromine, followed by basic peroxide led to the cis diol **14A** (45%). Reaction of the corresponding trans isomer **10B** under the same conditions led to formation of the corresponding trans diol **14B** (42%). These experiments establish that the tin cleavage reaction proceeds with overall retention of stereochemistry[8]. Presumably the second step of the reaction proceeds by way of nucleophilic attack of the peroxide anion at tin, giving the peroxystannane **12**, which undergoes a migration to the electrophilic center with retention of configuration giving alkoxystannane **13**, which converts to alcohol **14** upon hydrolysis. Alkyl migrations of this type are known to favor secondary groups over primary groups[9].

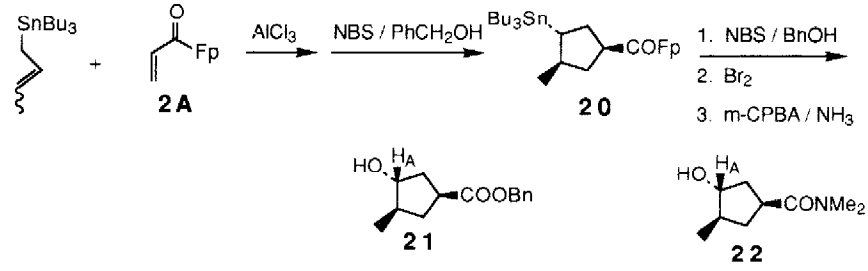
Having now established the conditions and stereoselectivity for the destannylation reaction, we now proceeded to destannylate select [3+2] cycloadducts from the cycloaddition reaction between allylstannanes and α,β–unsaturated acyliron complexes. Subjection of stannyl ester **4A** (Scheme 4) to the destannylation conditions reported previously gave alcohol **19A** in 57% yield[10]. This alcohol was identical to the minor isomer derived from reduction of keto ester **17A**. Phenylselenolactonization of the alkene **15A**, followed by reductive deselenation, hydrolysis, and esterification led to the major isomer from reduction of **17A**. This therefore establishes the relative stereochemistry of acyliron and tributyltin in **4A** as trans, which is in contrast to our earlier suggestion. Similarly, destannylation of ester **4B** led to a single alcohol in 79% yield. This product was not the isomer derived from phenylselenolactonization of **15B**, therefore establishing that the acyliron and

tributyltin groups were also trans to each other in the original cycloadduct **3B**. These results show that there is a preference for placing the tributyltin and acyliron groups trans in the [3+2] cycloaddition reaction.

Scheme 4



Scheme 5



Next, the stereochemistry of the substituents at other carbon atoms of the five-membered ring must be addressed. Reaction of crotyltributyltin (E:Z = 60:40) with iron complex **2A** led to a single diastereomer, assigned as **20** in 42% yield. Complete demetallation provided the ester-alcohol **21** in 67% overall yield. This compound exhibits chemical shifts and coupling patterns similar to compound **22**, which has previously been reported[11]. All possible stereoisomers of **22** have been prepared, and in compounds where the hydroxy and methyl substituents are trans, H_A exists as a quartet in the ^1H NMR spectrum and this proton is shielded upfield relative to the cis isomer or to compounds missing the methyl group. The observed relative stereochemistry between the tribuylstannyl and methyl groups is consistent with only the trans-crotylstannane participating in the cycloaddition reaction. Under the conditions of the reaction, cis-trans isomerization of the allylstannane could conceivably occur[12].

In summary, we have presented a method for the conversion of a tributyltin group at a secondary carbon atom into the corresponding alcohol. With these developments, the previously reported cycloaddition reaction between allylsytannanes and α,β-unsaturated acyliron complexes is now a useful method for the construction of highly substituted cyclopentane derivatives. Although the yields in the [3+2] cycloaddition reaction are somewhat less than optimal, the rapid formation of these compounds with high degrees of stereoselectivity make this a potentially powerful tool for the synthetic organic chemist.

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7. The following procedure was used for the conversion of bromostannanes to alcohols. To a flask containing an 0.3M solution of the bromostannane in CH_2Cl_2 at 0^oC was added a 2.0M solution of m-CPBA (2 - 3eq) in CH_2Cl_2. The mixture was allowed to stir 5 min at 0^oC, and ammonia gas was bubbled through the solution at ca 0.1 mL/min for 10 min. The mixture was then warmed to 25^oC, and extracted three times with saturated aqueous sodium carbonate solution, dried over sodium sulfate, and the solvent was removed on a rotary evaporator. Final purification was achieved by flash chromatography on silica gel. The yields were lower if triethylamine was substituted for ammonia or if peracetic acid was substituted for m-CPBA. In all cases, the reaction was performed on a scale of 0.1 - 1.8 g.

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10. ^1H NMR data for **19A**: δ 7.36 (br s, 5H); 5.11 (s, 2H); 4.46 (m, 1H); 3.12 (m, 1H); 1.70-2.22 (m, 6H); 1.65(br s, 1H). **19B**: δ 7.33(br s,5H); 5.08 (s, 2H); 4.40 (tt, 1H, J= 6.0, 3.9); 2.52 (dd, 1H, J = 14.0, 6.0); 1.63-2.20 (m, 5H); 1.49 (dd, 1H, J=14.0, 3.9); 1.40 (s, 3H). **21**: δ 7.34 (br s, 5 H); 5.10 (s, 2H); 3.84 (br q, 1H, J = 6.0); 3.04 (tt, 1H, J = 10.7, 7.4); 2.20 (m, 2H); 1.83 (m, 2H); 1.22 - 1.50 (m, 2H); 1.01 (d, 3H, J = 7.2).

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