CHEMISTRY LETTERS, pp. 985-988, 1988.

A Convenient Method for the Transformation of Allylstannanes to Alcohols, Ethers, Esters, and Amines

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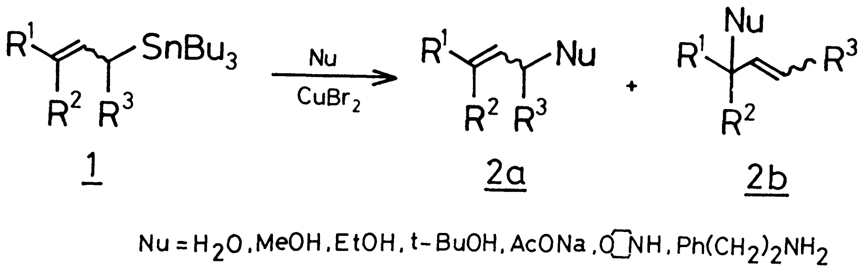
Allylstannanes were easily oxidized with copper(II) bromide in the presence of water, alcohols, and sodium acetate to give the corresponding allylic alcohols, ethers, and acetates, respectively. The allylic amines were also obtained by the successive treatments of allylstannanes with copper(II) bromide and amines.

Although much attention have been paid on the reactivity of organostannyl compounds and their utility in organic synthesis, few investigation was done for the oxidation of them.$^{1)}$ Concerning the generation of carbocation intermediate by the oxidation of organostannyl compound, Mizuno et al. recently reported that the treatment of benzylstannane with copper(II) tetrafluoroborate in the presence of alcohols under irradiation afforded benzyl ethers.$^{2)}$ This reaction is believed to proceed by the one electron transfer from the excited benzylstannane to copper(II) ion and the further oxidation of benzyl radical formed by the dissociation of initial radical cation intermediate with copper(II) salt.

In the previous paper, we reported a facile method for the regioselective transformation of allyl sulfides to allylstannanes (1) by the treatment with tributylstannyllithium in the presence of copper(I) bromide and hexamethylphosphoramide.$^{3)}$ In the course of the above investigation, we found that allylstannanes (1) were easily oxidized to produce an intermediate which had carbocationlike reactivity by the simple treatment with copper(II) halides in the appropriate solvents including water. This report summarizes our results of the study on the oxidative transformation of allylstannanes to the allylic compounds which have one single bond linking carbon to the heteroatom using copper(II) halides as oxidizing agent.



First we examined the transformation of 1 to the corresponding alcohols. When a THF solution of allylstannane (1) was added to the aqueous solution of 2 equiv. of copper(II) bromide at 0 °C, the greenish color of copper ion disappeared immediately and a white precipitate was deposited. After several hours, the corresponding allylic alcohols (2a and 2b) were obtained in good yields. Similarly, the allylic ethers were produced by the treatment of 1 with copper salt in alcohols. In the case of the reaction with amines and sodium acetate, the reaction was carried out in THF using 5 equiv. of nucleophile. Although the oxidation of allylstannane to the corresponding allylic alcohol or its derivative using m-chloroperbenzoic acid[4)] or thallium(III) salt[5)] was reported, the present method has advantages that the reaction is operationally simple and requires no toxic reagent.

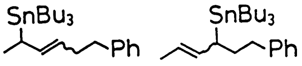
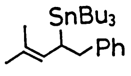
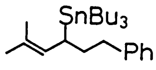
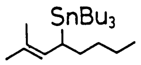
The typical experimental procedures are as follows: Procedure A; a EtOH (3 ml) suspension of $CuBr_2$ (246 mg, 1.1 mmol) was ultrasonicated for 15 min. 2-Methyl-4-(tributylstannyl)-6-phenyl-2-hexene (1f) (232 mg, 0.5 mmol) in THF and EtOH (1 ml each) was added to the suspension at 0 °C and the reaction mixture was stirred for 1 h. The reaction mixture was diluted with water and the organic material was extracted with CH_2Cl_2. The extract was washed with 10% KF aqueous solution, dried over Na_2SO_4, and condensed under reduced pressure. The residue was chromatographed on silica gel (hexane:AcOEt = 9:1) and 4-ethoxy-2-methyl-6-phenyl-2-hexene (2a)(66 mg, 60%) and 2-ethoxy-2-methyl-6-phenyl-3-hexene (2b)(36 mg, 33%) were isolated. Procedure B; after the ultrasonication of a THF (3 ml) suspension of $CuBr_2$ (246 mg, 1.1 mmol) for 15 min, a THF (2 ml) solution of 2-methyl-4-(tributylstannyl)-6-phenyl-2-hexene (1f) (232 mg, 0.5 mmol) was added to the suspension at -23 °C and the reaction mixture was stirred for 25 min. Then 2-phenylethylamine (303 mg, 2.5 mmol) in THF (1 ml) was added and the reaction mixture was gradually warmed up to r.t. After being stirred overnight, the reaction was quenched by addition of NaOH aqueous solution (1 mol dm^{-3}) and the usual work-up and purification (silica gel TLC, AcOEt) gave a mixture of N-(2-phenylethyl)-3-methyl-1-(2-phenylethyl)-2-propenylamine (2a) and N-(2-phenylethyl)-1,1-dimethyl-5-phenyl-2-propenylamine (2b)(120 mg) in 82% yield. The ratio of regioisomers (2a:2b = 15:85) was determined by HPLC analysis (Merck Si 60; solvent, hexane:AcOEt = 2:1).

In a similar manner, various allylic compounds (2) were prepared using several allylstannanes (1) and the results were summarized in the Table 1.

In the case of the reaction of the primary allylstannane (1b), it was found that the substituted product was obtained only in a poor yield but the corresponding allylic halide was produced as a main product by procedure B on account of the instability of the intermediate. The regioselectivity of the present reaction depends on the substituents of the allylic system of allylstannane and the nucleophile used. For example, the transformation of the trisubstituted allylstannanes (1e, 1f, and 1g) to the allylic alcohols afforded 2b as main products. On the other hand, 2a were preferentially produced by the reaction with alcohols under the similar reaction conditions. In general, the high regioselectivity was observed when the more reactive nucleophile (sodium acetate or amine) was used.

What is striking is a fact that the regioselectivity of the reaction of allylstannane (1f) with ethyl alcohol varied with the reaction temperature employed (Table 2); the reaction carried out using copper(II) bromide at -23 °C gave γ-substituted product (2b) with 84% selectivity, while 2a was produced selec-

Table 1. The preparation of allylic compounds (2) using allylstannanes (1)

Allylstannane (1)	Nucleophile (equiv.)	Procedure	Temp °C	Time h	Yield$^{b)}$ %	2a : 2b
 1a	H_2O	A	r.t.	6	61	33 : 67$^{c)}$
	EtOH	A	0-r.t.	overnight	80	46 : 54$^{c)}$
 1b	H_2O	A	r.t.	2	86	26 : 74$^{c)}$
	EtOH	A	0-r.t.	overnight	85	18 : 82$^{c)}$
	t-BuOH	A	30	overnight	76	74 : 26$^{c)}$
	AcONa(5)	A	0-r.t.	overnight	42	<5 :>95$^{d)}$
 1c	$PhCH_2OH$	A	r.t.	overnight	61	56 : 44$^{c)}$
 1d a)	H_2O	A	r.t.	4	56	34 : 66$^{c,e)}$
	MeOH	A	r.t.	overnight	80	34 : 66$^{c,e)}$
 1e	H_2O	A	r.t.	5	69	18 : 82$^{d)}$
	MeOH	A	0	overnight	93	81 : 19$^{c)}$
	EtOH	A	0-r.t.	overnight	87	76 : 24$^{c)}$
	morpholine(5)	B	-23-r.t.	overnight	71	<5 :>95$^{d)}$
	$Ph(CH_2)_2NH_2(5)$	B	-23-r.t.	overnight	73	7 : 93$^{d)}$
 1f	H_2O	A	r.t.	2	82	19 : 81$^{d)}$
	MeOH	A	r.t.	overnight	82	75 : 25$^{c)}$
	AcONa(5)	A	r.t.	overnight	62	<5 :>95$^{d)}$
	morpholine(5)	B	-23-r.t.	overnight	75	<5 :>95$^{d)}$
	$Ph(CH_2)_2NH_2(5)$	B	-23-r.t.	overnight	82	15 : 85$^{f)}$
 1g	H_2O	A	r.t.	4	65	29 : 71$^{d)}$
	EtOH	A	0	5	73	83 : 17$^{d)}$
	$Ph(CH_2)_2NH_2(5)$	B	-23-r.t.	overnight	73	14 : 86$^{d)}$

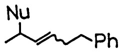
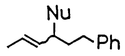
a) The mixture of regioisomers. b) All products were identified by IR and NMR spectra. c) Based on the yields of the isolated regioisomers. d) Determined by NMR spectrum. e)  :  f) Determined by HPLC analysis (Merck Si 60; solvent, Hexane-AcOEt (2:1)).

Table 2. The transformation of the allylstannane (1f) to allylic ethers (2)

CuX_2 (2.2 equiv.)	Additive (2.2 equiv.)	Temp °C	Time h	Yield %	2a : 2b
$CuBr_2$	-	0	1	93	65 : 35
$CuBr_2$	-	-23	4	69	16 : 84
$CuCl_2$	-	0	3	71	69 : 31
$CuCl_2$	-	-23	5	74	27 : 73
$CuBr_2$	NaI	0	overnight	72	86 : 14
$CuCl_2$	NaI	0	overnight	93	77 : 23

tively (86% selectivity) by the treatment of 1 with copper(II) bromide in the presence of NaI at 0 °C.

Although the alkylation of allyl sulfides is one of the most important methods for the formation of carbon-carbon bond, the introduction of a certain functional group to the alkylated allyl sulfides with desulfurization is generally difficult except for the desulfurizative reduction to the corresponding hydrocarbons$^{6)}$ or the rearrangement to alcohols after allyl sulfides are converted to sulfoxides.$^{7)}$ Since the substituted allyl sulfides are easily transformed to the corresponding allylstannanes, the present reaction provides a useful method for the desulfurizative functionalization of substituted allyl sulfides.

Further study including the investigation of the reaction path way is now in progress.

References

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(Received April 1, 1988)