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The Oxidative Coupling Reaction of Allylstannanes with Trimethylsilyl Enol Ethers

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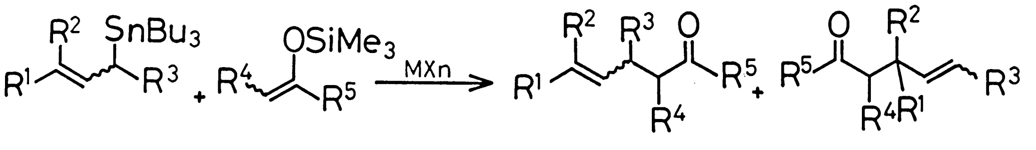
γ,δ-Unsaturated ketones were obtained by the reaction of trimetylsilyl enol ethers with allylstannanes in the presence of tin(IV) or copper(II) salt in good yields.

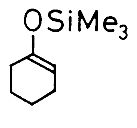
The introduction of substituted allyl group is one of the most important processes for the synthesis of natural products and various reactions utilizing organometallic compounds have been investigated. Recently the use of allylstannane (1) as a reagent for allylation has been extensively studied because of its distinctive reactivity. The reactions of 1 reported are divided broadly into three categories; (1) Transmetallation and following reaction with an electrophile.[1] (2) Lewis acid or transition metal complex-promoted reaction with an electrophile.[2] (3) Reaction via a radical intermediate.[3] However, few investigations were done for the oxidative transformation of 1 to an intermediate which has carbocationlike reactivity.[4]

In the previous paper,[5] we showed that allylstannanes (1) are easily transformed to the various allylic compounds such as alcohols, ethers, and amines by the oxidation with copper(II) salts in the presence of the corresponding nucleophiles. These results suggest that the possibility of another type of reactions still remains in allylstannane chemistry. In this communication, we wish to report a new method for the allylation of ketones, which consists of the oxidation of allylstannane (1) with copper(II), tin(IV), or titanium(IV) salt and the reaction of trimethylsilyl enol ether with the resulting active species (Eq 1).

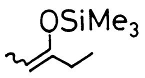


(1)

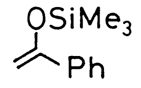
1 2 3a 3b



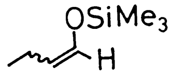
2a



2b



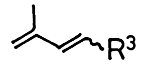
2c



2d

(R^2=R^3=H)

4



(R^1=R^2=CH$_3$)

5

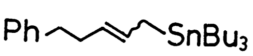
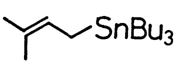
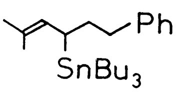
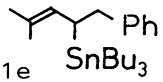
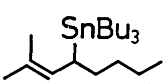
The oxidation of allylstannane (1) was carried out in the presence of trimethylsilyl enol ether (2) so that the intermediate formed could react with 2 before it decomposed to the corresponding halide (4) or diene (5). When primary allylstannanes (1a, 1b, 1c) were treated with copper(II) bromide in the presence of trimethylsilyl enol ethers, the coupling products, γ,δ-unsaturated ketones (3), were produced in good to moderate yields. Although the formation of allyl halide (4) became a serious side reaction in certain cases, copper(II) triflate or trifluoroacetate was found to be effective in such reactions. On the other hand, the coupling products (3) were obtained in good to high yields by the reaction of the secondary allylstannanes (1d, 1e, 1f) using tin(IV) chloride as an oxidizing agent. In the case of the reaction of 1d using copper(II) bromide, the yield of the coupling product decreased in general (run 12) and a substantial amount of diene (5) was produced.

In the reaction of primary allylstannanes (1a, 1b, 1c), trimethylsilyl enol ethers attacked at the less substituted side of an allyl system to give the α-coupling products (3a) selectively. On the other hand, the ratio of the two regioisomers varied with the oxidant (runs 12 and 13), the substituents on both allylstannane (1) (runs 11 and 16) and trimethylsilyl enol ether (2) (runs 16 and 17, for example), and moreover the amount of 2 used (runs 13 and 14) when secondary allylstannanes (1d, 1e, 1f) were employed. These results are summarized in the Table.

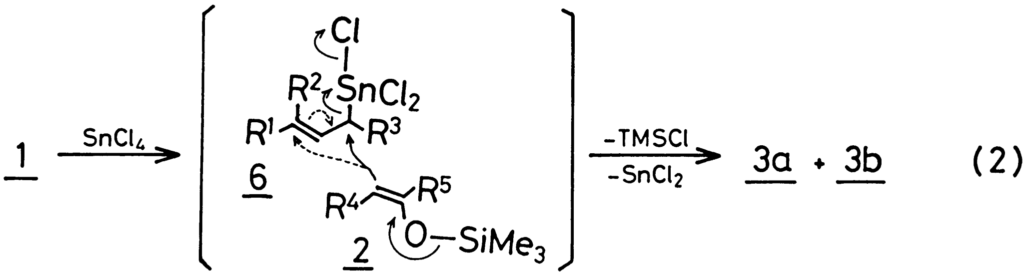
A typical experimental procedures are as follows: Procedure A; to a benzene (3 ml) suspension of copper(II) trifluoroacetate (319 mg, 1.1 mmol) and molecular sieves 3A (0.5 g) was added a benzene solution of 1-(tributylstannyl)-5-phenyl-2-pentene (1a) (218 mg, 0.5 mmol) and 1-(trimethylsiloxy)cyclohexene (2a) (170 mg, 1 mmol) at r.t. After being stirred for one day, the reaction was quenched by addition of 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 = 95 : 5) and then 2-(5-phenyl-2-pentenyl)cyclohexanone (3a) (70 mg, 58%) was obtained. Procedure B; to a CH_2Cl_2 (3 ml) solution of 4-(tributylstannyl)-2-methyl-6-phenyl-2-hexene (1d) (232 mg, 0.5 mmol) and 1-(trimethylsiloxy)cyclohexene (2a) (170 mg, 1 mmol) was added a CH_2Cl_2 (0.52 ml) solution of $SnCl_4$ (1.1 mmol) at -78 °C. After being stirred for 1.5 h, the reaction was quenched by addition of water. The usual work-up and purification (silica gel TLC, Hexane : AcOEt = 95 : 5) gave 2-[1-(2-phenylethyl)-3-methyl-2-butenyl]cyclohexanone (3a) (60 mg, 44%) and 2-(1,1-dimethyl-5-phenyl-2-pentenyl)cyclohexanone (3b) (60 mg, 44%).

Although the pathway of the reaction using copper(II) salts as an oxidizing agent is not clear at present, we assume that the reaction using tin(IV) chloride proceeds through initial formation of allyltrichlorostannane (6).[6] Then the coupling product (3) is produced by the nucleophilic attack of trimethylsilyl enol ether and the simultaneous elimination of tin(II) chloride as illustrated below. Since allyltrichlorostannane (6) is proved to be an active intermediate in the reaction of allylstannane (1) with aldehyde in the presence of $SnCl_4$,[6] it is of interest that 6 possesses both nucleophilic and electrophilic reactivities toward carbonyl compounds and their derivatives.

Table 1. The reaction of allylstannanes (1) with trimethylsilyl enol ethers (2) a)

Run	1	2	MX_n	Solvent	Temp °C	Time h	Yield b) %	3a : 3b c)
1	 1a	2a	$Cu(OCOCF_3)_2$	PhH	r.t.	1 day	58	>95 : <5
2		2b	$Cu(OCOCF_3)_2$	PhH	r.t.	1 day	54	>95 : <5
3		2c	$CuBr_2$	$CHCl_3$	-25 ~ r.t.	overnight	57	>95 : <5
4		2c	$SnCl_4$	CH_2Cl_2	-78	0.5	0	
5	 1b	2b	$Cu(OCOCF_3)_2$	PhH	r.t.	2 days	57	>95 : <5
6		2c	$CuBr_2$	$CHCl_3$	-25 ~ r.t.	overnight	74	>95 : <5
7	 1c	2b	$Cu(OTf)_2$	PhH	r.t.	2 days	54	>95 : <5
8		2c	$CuBr_2$	PhH	10	0.8	70	74 : 26
9	 1d	2a	$TiCl_4$	CH_2Cl_2	-78	0.15	90	57 : 43 d)
10		2a	$SnCl_4$	CH_2Cl_2	-78	1.5	88	50 : 50 d)
11		2b	$SnCl_4$	CH_2Cl_2	-78	0.1	98	41 : 59 d)
12		2c	$CuBr_2$	CCl_4	0 ~ r.t.	1.3	46	38 : 62
13		2c	$SnCl_4$	CH_2Cl_2	-78	0.5	88	53 : 47
14 e)		2c	$SnCl_4$	CH_2Cl_2	-78	2.5	46	14 : 86
15		2d	$CuBr_2$	CH_2Cl_2	-30 ~ -13	1.8	76	52 : 48
16	 1e	2a	$SnCl_4$	CH_2Cl_2	-78	0.25	78	18 : 82
17		2b	$SnCl_4$	CH_2Cl_2	-78	0.5	86	43 : 57
18		2c	$SnCl_4$	CH_2Cl_2	-78	0.25	69	37 : 63
19	 1f	2a	$SnCl_4$	$CHCl_3$	-60	1	57	31 : 69
20		2c	$SnCl_4$	PhH	7	1	69	63 : 37

a) All the reactions were performed with a similar procedure as described in the text, unless otherwise noted. b) The structures of these compounds were supported by IR and NMR spectra. c) Determined by NMR spectrum, unless otherwise noted. d) Based on the yields of the isolated regioisomers. e) 1.2 equiv. of 2c were used.



(2)

Concerning the allylation of trimethylsilyl enol ether (2), Paterson reported that the reaction of prenyl bromide with 2 in the presence of $ZnCl_2$ gave 2-prenylketones.$^{7)}$ However, this method inevitably suffers some limitations owing to the difficulty of preparation and instability of allylic halides.$^{8)}$ As allylstannanes (1) are stable enough to be stored even in the case of highly substituted ones and easily prepared from the corresponding allylic sulfides,$^{9)}$ acetates,$^{10)}$ and phosphates,$^{11)}$ the present reaction provides a convenient method for the allylation of ketones.

References

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