Nickel-Catalyzed Acylstannylation of 1,3-Dienes: Synthesis and Reaction of ϵ-Oxoallylstannanes

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Allylstannanes are one of the most versatile synthetic reagents that react with electrophilic substrates such as carbonyl compounds and organic halides to give a variety of olefinic products.[1] Although unsubstituted allylstannanes are readily prepared by the reaction between allyl/stannyl nucleophilic/electrophilic reagents, no convenient and general methods are available for the synthesis of functionalized allylstannanes. Here we report that the nickel-catalyzed 1,4-acylstannylation of 1,3-dienes provides a convenient method for the synthesis of allylstannanes having a carbonyl group.[2] To the best of our knowledge, this is the first example of the transition metal-catalyzed carbometalation of 1,3-dienes at their 1,4-positions except for the allylmagnesation of 1,3-dienes[3] and the carbosilylation through three component coupling of 1,3-dienes, disilanes and acyl chlorides.[4]

We first examined the reaction of benzoyl(trimethyl)tin (**1a**) with 1,3-butadiene (**2a**) in the presence of a nickel complex and found that PhCO and $SnMe_3$ moieties in **1a** were delivered to **2a** at its 1,4-positions. For example, treatment of **1a** and **2a** with 5 mol% of $Ni(cod)_2$ in toluene at 50 °C for 10 min gave (*Z*)-1-phenyl-5-trimethylstannyl-3-penten-1-one (**3a**)[5] in 72% yield (Scheme 1 and entry 1 of Table 1).[6] 2,3-Disubstituted 1,3-butadienes **2b**−**d** also reacted with **1a** stereoselectively to give the corresponding allylstannanes (entries 2−4). The addition of **1a** to 2-substituted 1,3-dienes afforded corresponding products as mixtures of regioisomers (entries 5−8). Propanoylstannane **1b** and 3-methyl-2-butenoylstannane **1c** added to **2b**, giving acylstannylation products as a single isomer (entries 9 and 10), whereas a mixture of stereoisomers was obtained in the reaction of piperidinocarbonylstannane **1d** (entry 11).

Solvent was found to strikingly affect the selectivity of the reaction of **1a** with **2b**: the acylstannylation versus decarbonylation of an acylstannane. The fraction of the decarbonylation was less than 15% in such a nonpolar solvent as toluene or octane, whereas a polar solvent DMF or THF predominantly caused the decarbonylation to give trimethyl(phenyl)tin (**5a**) in more than 80% yield. In the absence of a 1,3-diene even in toluene, **1a** afforded **5a** in 56% yield (eq 1).

Scheme 1

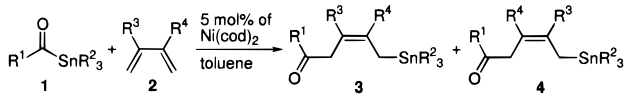
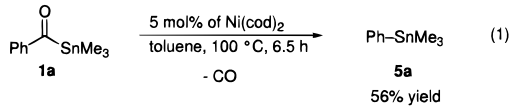


Table 1. Nickel-Catalyzed Acylstannylation of 1,3-Dienes[a]

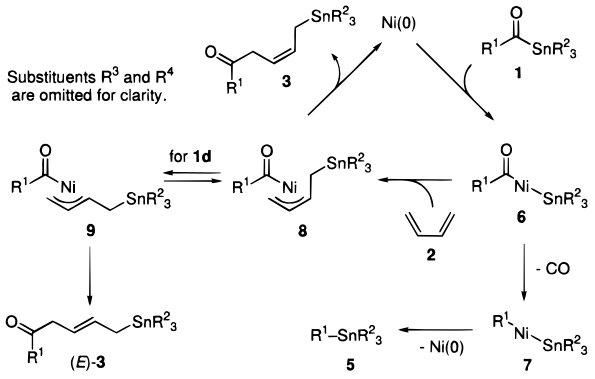
	acylstannane		1,3-diene		time	yield	prod(s),
entry	R^1	R^2	R^3	R^4	(h)	(%)[b]	**3**:**4**[c]
1	Ph	Me (**1a**)	H	H (**2a**)	0.2	72	**3a** −
2	Ph	Me (**1a**)	Me	Me (**2b**)	2	73	**3b** −
3[d]	Ph	Me (**1a**)	Ph	Ph (**2c**)	48	36	**3c** −
4[e]	Ph	Me (**1a**)	−$(CH_2)_4$− (**2d**)		24	45	**3d** −
5	Ph	Me (**1a**)	Me	H (**2e**)	2	74	**3e**, **4e** 33:67
6	Ph	Me (**1a**)	Ph	H (**2f**)	2	68	**3f**, **4f** 47:53
7	Ph	Me (**1a**)	$SiMe_3$	H (**2g**)	2	84	**3g**, **4g** 44:56
8	Ph	Me (**1a**)	CH_2SiMe_3	H (**2h**)	2	86	**3h**, **4h** 39:61
9[e]	Et	Bu (**1b**)	Me	Me (**2b**)	24	56	**3i** −
10[e]	Me_2C=CH	Bu (**1c**)	Me	Me (**2b**)	2	52	**3j** −
11	$(CH_2)_5N$	Bu (**1d**)	Me	Me (**2b**)	2	73	**3k**[f] −

[a] The reaction was carried out in toluene (0.3 mL) at 50 °C using an acylstannane (0.23 mmol), a 1,3-diene (0.69 mmol) and $Ni(cod)_2$ (11.5 μmol). [b] Isolated yield based on the organostannane. [c] Determined by ^{119}Sn NMR. [d] Reaction was carried out at 80 °C. [e] Reaction was carried out at 70 °C. [f] A 87:13 mixture of (*Z*)- and (*E*)-isomers was obtained.



The decarbonylation of **1a** is attributed to oxidative addition of **1a** to the nickel(0) complex followed by deinsertion of carbon monoxide from complex **6** and reductive elimination of **5a** from **7** as illustrated in Scheme 2. This fact suggests that the acylstannylation of 1,3-dienes should be initiated by the oxidative addition to give **6**, followed by insertion of a 1,3-diene to the Ni−Sn bond in **6**, affording π-allylnickel complex **8**,[7] which then undergoes reductive elimination to give rise to **3** (Scheme 2).

Scheme 2



† Japan Advanced Institute of Science and Technology.
‡ Kyoto University.

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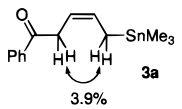
(4) (a) Obora, Y.; Tsuji, Y.; Kawamura, T. *J. Am. Chem. Soc.* **1993**, *115*, 10414−10415. (b) Obora, Y.; Tsuji, Y.; Kawamura, T. *J. Am. Chem. Soc.* **1995**, *117*, 9814−9821.

(5) Configuration of the carbostannylation products was determined by NOE in ^{1}H NMR as is shown below.



(6) The reaction conditions are essentially identical with those used in the nickel-catalyzed carbostannylation of alkynes, see ref 2c.

(7) A similar catalytic cycle involving an *anti*-π-allylplatinum intermediate generated by insertion of a 1,3-diene to a Pt−B bond is proposed in the platinum-catalyzed diboration of 1,3-dienes. Ishiyama, T.; Yamamoto, M.; Miyaura, N. *Chem. Commun.* **1996**, 2073−2074.

10.1021/ja0020409 CCC: $19.00
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Scheme 3

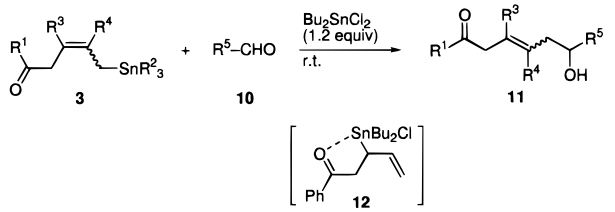


Table 2. Addition of Allylstannanes to Aldehydes Mediated by Bu_2SnCl_2[a]

entry	allylstannane	R^5	time (h)	yield (%)[b]	prod	*E*:*Z*
1	**3a**	*i*-Pr	3.5	67	**11a**	87:13
2	**3a**	Ph[c]	3.5	76	**11b**	89:11
3	(*Z*)-**3k**	*i*-Pr	2.0	98	**11c**	>99:1
4	(*E*)-**3k**	*i*-Pr	2.0	100	**11c**	>99:1

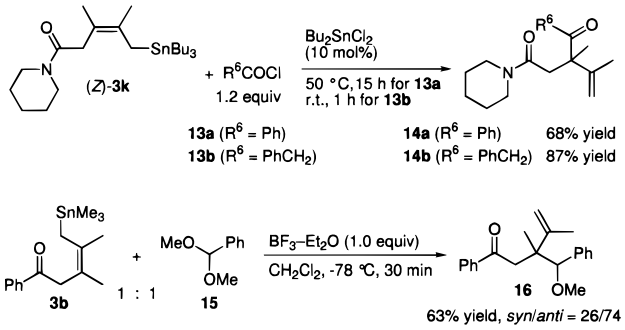
[a] The reaction was carried out at room temperature using an allylstannane (0.30 mmol), an aldehyde (0.60 mmol) and Bu_2SnCl_2 (0.36 mmol). [b] Isolated yield based on the allylstannane. [c] Benzaldehyde (0.36 mmol) was used.

In the case of aminocarbonylstannane **1d**, isomerization of π-allylnickel complex **8** to **9** before reluctant reductive elimination may cause coproduction of stereoisomer (*E*)-**3k**. The stannylnickelation pathway, as compared with an alternative carbonickelation pathway, more likely explains the fact that the difference in the acyl moieties largely affects the stereochemical results.

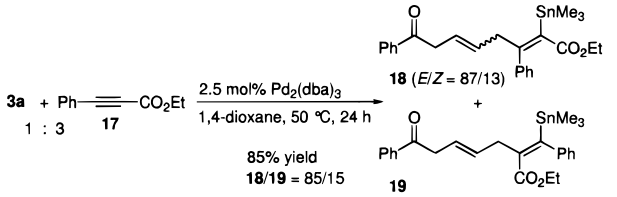
The acylstannylated products are applicable to the synthesis of various olefinic compounds by the reaction with diverse kinds of electrophiles. The addition of allylstannane **3a** to 2-methylpropanal (**10a**), after transmetalation with dibutyltin dichloride, afforded homoallyl alcohol **11a** in 67% yield, the carbon−carbon bond formation occurring exclusively at the α-carbon of **3a** (Scheme 3 and entry 1 of Table 2), in striking contrast to tributyl(crotyl)tin which upon the reaction with **10a** gives an 87:13 mixture of α- and γ-adducts.[8] The exclusive α-selectivity observed with **3a** should be ascribed to intramolecular coordination of the carbonyl group to the γ-tin atom, which stabilizes intermediate **12**[9] to induce the carbon−carbon bond formation at the terminal carbon. **3a** reacted also with benzaldehyde (**10b**) to give linear homoallyl alcohol **11b** in 76% yield (entry 2). It is noteworthy that the carbonyl group in allylstannanes **3a** precisely controls the regioselectivity of the reaction. Both of stereoisomers (*Z*)-**3k** and (*E*)-**3k** in combination with dibutyltin dichloride reacted with **10a** to afford **11c** as a single isomer (entries 3 and 4).[10]

In the presence of 10 mol% of dibutyltin dichloride, (*Z*)-**3k** reacted with benzoyl chloride (**13a**) or phenylacetyl chloride (**13b**) to give γ-acylated product regioselectively (Scheme 4), whereas the corresponding reaction of tributyl(crotyl)tin with the aid of 15 mol% of Et_4NCl is reported to provide no adduct for **13a** or

Scheme 4



Scheme 5



a mixture of α- and γ-adducts (41:59, 75% yield) for **13b**.[11] The intramolecular oxygen-to-tin coordination in the reaction of (*Z*)-**3k** should be responsible for high reactivity and high regioselectivity, although the reason the reaction with acyl chlorides showed the regiochemical result opposite from that with aldehydes is not clear at present. The nucleophilic attack of **3b** to benzaldehyde dimethyl acetal (**15**) activated by BF_3-OEt_2 proceeded with exclusive γ-selectivity, affording *syn*- and *anti*-branched ethers **16** in a ratio of 26:74.[12]

Combination of the acylstannylation of 1,3-dienes and allylstannylation of alkynes should be a versatile method for the preparation of alkenylstannanes having a functional group requisite for further synthetic elaborations. Indeed, acylstannylation product **3a** derived from 1,3-diene **2a** was allowed to add to ethyl phenylpropiolate (**17**) in the presence of a palladium catalyst to give acyldienylstannanes **18** and **19** in 85% yield (Scheme 5).[2d]

In conclusion, we have demonstrated that acylstannylation of 1,3-dienes proceeded in a high stereoselectivity in the presence of a nickel catalyst. Furthermore, the resulting ϵ-oxoallylstannanes were transformed to various unconjugated enones in many ways by virtue of the carbonyl group playing a significant role. Further studies on the synthetic application of the reaction as well as carbostannylations using various organostannanes and unsaturated compounds are in progress in our laboratories.

Acknowledgment. We are grateful to Dr. Yasushi Nishihara, Tokyo Institute of Technology, for the X-ray crystal structure analysis. We thank Denkikagaku Kogyo Co., Ltd. for the generous gift of chloroprene.

Supporting Information Available: Detailed experimental procedures including spectroscopic and analytical data (PDF). An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http:/pubs.acs.org.

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(10) Configuration of **11c** was determined by NOE in a manner similar to that depicted in ref 5.

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(12) The relative configuration was determined by an X-ray crystal structure analysis of *anti*-**16**, see Supporting Information.