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Nickel-catalysed acylstannylation of 1,2-dienes: synthesis and reactions of α-(acylmethyl)vinylstannanes

Eiji Shirakawa,*[a] Yoshiaki Nakao[b] and Tamejiro Hiyama*[b]

[a] *Graduate School of Materials Science, Japan Advanced Institute of Science and Technology, Asahidai, Tatsunokuchi, Ishikawa, 923-1292, Japan*

[b] *Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto, 606-8501, Japan*

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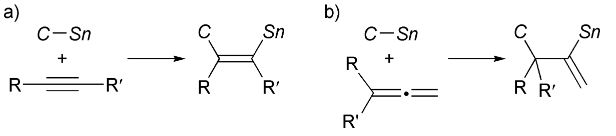
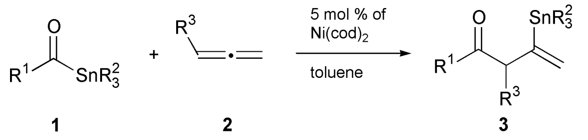
Bis(cycloocta-1,5-diene)nickel was found to be an effective catalyst for the acylstannylation of 1,2-dienes to give a wide variety of α-(acylmethyl)vinylstannanes, which were transformed to variously substituted conjugated and unconjugated enones by carbon–carbon bond forming reactions.

Alkenylstannanes are one of the most versatile synthetic reagents, since they can be transformed to various olefinic compounds through the reaction with organic electrophiles, *e.g.* the palladium-catalysed cross-coupling reaction.[1] Although the reaction of other alkenylmetals with stannyl halides provides an easy access to alkenylstannanes, this synthetic method cannot be applied to those having such a reactive substituent as carbonyl. Carbostannylation of alkynes has grown to be a powerful alternative route to alkenylstannanes, especially multi-substituted vinylstannanes (Scheme 1, a).[2] Herein we disclose that acylstannanes add to 1,2-dienes in the presence of a nickel catalyst[3] to give α-(acylmethyl)vinylstannanes[4] as main products (Scheme 1, b) and the resulting alkenylstannanes can be transformed to variously conjugated and/or unconjugated enones. To the best of our knowledge, this is the first demonstration of the transition metal-catalysed addition of a carbon–metal bond of organometallic compounds to 1,2-dienes.[5,6]



Scheme 1

Acylstannylation of monosubstituted allenes were carried out in the presence of a nickel catalyst (Scheme 2 and Table 1). The following procedure is representative (entry 1). A mixture of trimethyl(benzoyl)tin (**1a**) and 5 mol% of Ni(cod)$_2$ in toluene was heated at 50 °C for 1.5 h under an atmosphere of propa-1,2-diene (**2a**) to give 1-phenyl-3-trimethylstannylbut-3-en-1-one (**3a**) in 64% yield.[7] Analysis of the reaction mixture by ^{119}Sn NMR revealed that the ratio of **3a** and (*E*)-1-phenyl-3-trimethylstannylbut-2-en-1-one, derived probably through the isomerization of **3a**, was 97:3, although trimethyl(phenyl)tin, the decarbonylated product of **1a**, was obtained in a small amount. Addition of **1a** to hepta-1,2-diene (**2b**) took place mainly at the internal C–C double bond to give **3b** in 79% yield (entry 2).[8] Similar regioselectivity was observed in the reaction of 4,4-dimethylpenta-1,2-diene (**2c**) (entry 3). Arylallenes also participated in the acylstannylation with the selectivity of **3** being lowered by an electron-withdrawing substituent on the aromatic ring (entries 4–6). The reaction of 1-methoxypropa-1,2-diene (**2g**) proceeded with the benzoyl group of **1a** adding mainly at the carbon having the methoxy group albeit in a low yield (entry 7). The tributylstannyl derivative (**1b**) of **1a** also gave the acylstannylated product (entry 8). Tributyl(propanoyl)tin (**1c**) also added to various 1,2-dienes (entries 9–12). Noteworthy is that **2g** reacted with **1c** better than with **1a** to afford acylstannylation product **3l** in a higher yield. Aminocarbonylstannane **1d** reacted with allene (**2a**) in a low yield (entry 13).



Scheme 2

Disubstituted allenes also participated in the acylstannylation (Scheme 3). Acylstannanes **1a** and **1c** added to 3-methylbuta-1,2-diene (**2h**) with high regioselectivities. In addition, nona-4,5-diene (**2i**) also underwent the reaction, giving a stereoisomeric mixture of **3p** or **3q**.

The catalytic cycle is considered to be initiated by the oxidative addition of an acylstannane to a nickel(0) complex as is the case with the nickel-catalysed acylstannylation of 1,3-dienes, since the decarbonylation of acylstannanes was similarly observed as a side reaction.[3] Although the succeeding pathway remains yet to be clarified, two plausible catalytic cycles leading to the main products are presented in Scheme 4. In any event, the stannyl group invariably attacks the allene central carbon. In Cycle A, coordination of the less hindered double bond of 1,2-diene **2** on the nickel atom of oxidative adduct **4** followed by insertion to the Ni–Sn bond (stannylnickelation) affords the acylstannylation product through π-allylnickel complex **6**. According to Cycle B, the more hindered double bond of **2** coordinates on the nickel and then inserts to

Table 1 Nickel-catalysed acylstannylation of 1,2-dienes[a]

	Acylstannane		1,2-Diene	Time/	Yield of	Prod **3**:	
Entry	R^1	R^2	R^3	h	**3** (%)[b]	others[c]	
1[d]	Ph	Me (**1a**)	H (**2a**)	1.5	64	**3a**	97:3
2	Ph	Me (**1a**)	Bu (**2b**)	1.5	79	**3b**	89:11
3	Ph	Me (**1a**)	*t*-Bu (**2c**)	1.5	59	**3c**	86:14
4	Ph	Me (**1a**)	4-MeOC$_6$H$_4$ (**2d**)	2	50	**3d**	78:22
5	Ph	Me (**1a**)	Ph (**2e**)	2	53	**3e**	77:23
6	Ph	Me (**1a**)	4-CF$_3$C$_6$H$_4$ (**2f**)	2	35	**3f**	66:34
7	Ph	Me (**1a**)	MeO (**2g**)	2	26	**3g**	93:7
8[d]	Ph	Bu (**1b**)	H (**2a**)	4	48	**3h**	79:21
9[d]	Et	Bu (**1c**)	H (**2a**)	1.5	67	**3i**	94:6
10[e]	Et	Bu (**1c**)	Bu (**2b**)	2	53	**3j**	89:11
11[e]	Et	Bu (**1c**)	Ph (**2e**)	3.5	43	**3k**	79:21
12[e]	Et	Bu (**1c**)	MeO (**2g**)	2.5	48	**3l**	95:5
13[d,f]	(CH$_2$)$_5$N	Me (**1d**)	H (**2a**)	2	25	**3m**	—[g]

[a] The reaction was carried out in toluene (0.4 mL) at 50 °C using an acylstannane (0.30 mmol), a 1,2-diene (0.90 mmol) and Ni(cod)$_2$ (15 μmol). [b] Isolated yield based on the organostannane. [c] Determined by ^{119}Sn NMR. [d] The reaction was carried out under an allene atmosphere (1 atm). [e] The reaction was carried out at 80 °C. [f] The reaction was carried out at 100 °C in the presence of 60 μmol of Ni(cod)$_2$. [g] Accompanied by a complex mixture of the products other than **3m**.

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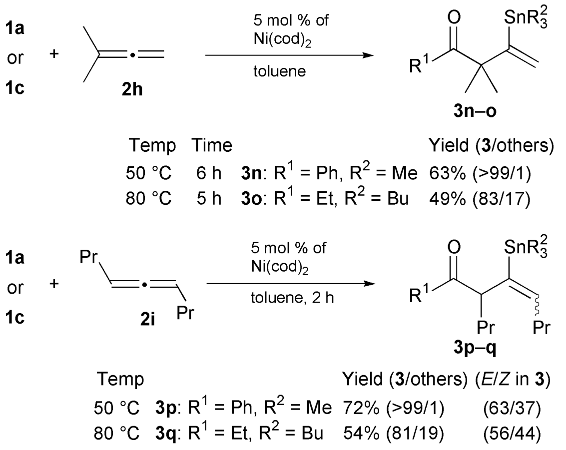
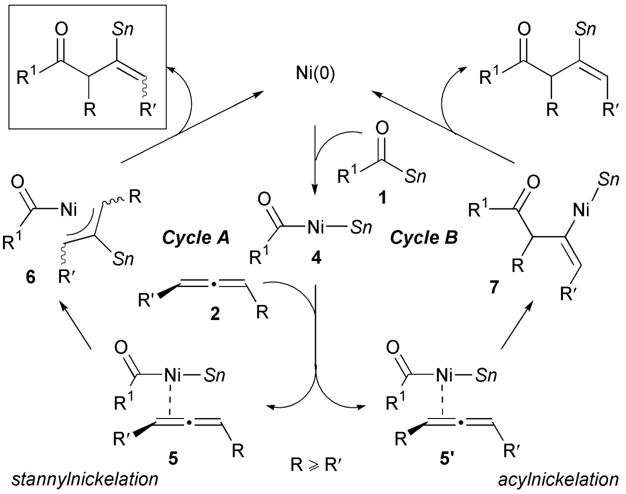


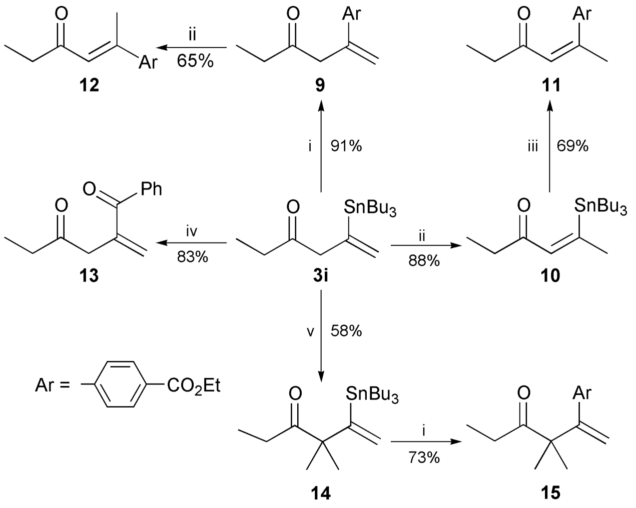
Scheme 3

the C–Ni bond of **4** (acylnickelation), giving the product *via* alkenylnickel **7**.[9] The results that the acylstannylation of nona-4,5-diene (**2i**) gave a mixture of stereoisomers should give us a clue to discriminate the reaction mechanism. In the case that the reaction with **2i** follows Cycle B, only (*E*)-**3p** or **3q** should be provided through *syn*-addition of the C–Ni bond to the C–C double bond and stereo-retained reductive elimination. As this was not the case, Cycle A appears to be more plausible, although it is unclear yet why reductive elimination from **6** takes place mainly at the more hindered carbon of the allyl moiety.



Scheme 4

The applicability of the acylstannylation products was demonstrated by the transformation of **3i** to a wide variety of enones (Scheme 5). The reaction of **3i** with ethyl 4-iodobenzoate (**8**) in the presence of 2.5 mol% of $Pd_2(dba)_3$ gave the corresponding coupling product **9** in 91% yield[10] without cine-substitution.[1b] Conjugated β-arylenone **11** was obtained[11] by cross-coupling reaction with **8** after isomerization of **3i** to **10** by 20 mol% of sodium hydride, whereas the corresponding (*E*)-isomer **12** was obtained by base-catalysed isomerization of **9**. The cross-coupling of **3i** with benzoyl chloride proceeded to give 83% yield of enedione **13**. Stannylenone **3i** reacted with iodomethane in the presence of sodium hydride, giving dimethylation product **14**, which was subjected to the cross-coupling reaction with **8** to afford arylenone **15**. Thus, variously substituted conjugated and unconjugated enones were synthesized from a single acylstannylation product.



Scheme 5 *Reagents and conditions*: i, 4-EtOCO–C_6H_4–I (**8**, 1.0 equiv), 2.5 mol% of $Pd_2(db\ a)_3$, NMP, 30 °C, 15 h (from **3i** to **9**) or 10 h (from **14** to **15**); ii, NaH (0.2 equiv.), THF, rt, 4 h (from **3i** to **10**) or 3 h (from **9** to **12**); iii, **8** (1.0 equiv.), 5 mol% of $Pd_2(dba)_3$, NMP, 30 °C, 69 h; iv, PhCOCl (1.0 equiv.), 2.5 mol% of $Pd_2(dba)_3$, NMP, 30 °C, 8 h; v, Me–I (3.0 equiv.) THF, rt, 17 h.

In conclusion, we have demonstrated that the acylstannylation of 1,2-dienes readily takes place to give α-(acylmethyl)-vinylstannanes, which were transformed to a wide variety of conjugated and unconjugated enones. Studies on details of the mechanism as well as synthetic applications to various unsaturated substrates and organostannanes are in progress in our laboratories.

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6 The palladium-catalysed three component coupling of 1,2-dienes, distannanes and organic iodides is reported to provide allylstannanes: F.-Y. Yang, M.-Y. Wu and C.-H. Cheng, *Tetrahedron Lett.*, 1999, **40**, 6055.
7 The reaction conditions are essentially identical with those used in the nickel-catalysed carbostannylation of alkynes, see ref. 2e.
8 The reaction mixture contains 2-methylene-1-phenyl-3-trimethylstannylheptan-1-one (5% yield) and (*E*)-1-phenyl-3-trimethylstannyloct-3-en-1-one (4% yield). Although we did not characterize the minor isomer(s) in the following entries thoroughly, peak(s) in ^{119}Sn NMR was always observed at −42.2 to 14.2 ppm, being attributed to an alkenyl- or allyl(trialkyl)stannane.
9 Platinum-catalysed diboration of monosubstituted allenes, which is considered to proceed *via* an alkenylplatinum complex similar to **7**, gave the (*Z*)-isomer stereoselectively. T. Ishiyama, T. Kitano and N. Miyaura, *Tetrahedron Lett.*, 1998, **39**, 2357.
10 Conjugated arylenone **12** was also generated in 5% yield.
11 The reaction mixture contains **12** (8% yield).