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Homolytic allylation of vinyl iodides with allylstannanes

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Abstract

In the presence of AIBN or Et_3B, a variety of vinyl iodides reacted with allylstannanes bearing an electron-withdrawing group at the β-position to afford 1,4-dienes in moderate to good yields. The allylation showed high stereoselectivity when the α-substituent of the iodides was a phenyl group, or the β-substituent was a bulky group.

Keywords: allylation; radicals; radical reactions; tin; tin compounds; dienes.

Inter- and intramolecular addition reactions of carbon-centered radicals to unsaturated carbon–carbon and carbon-hetero atom bonds have been widely utilized for carbon–carbon bond formation.[1,2] However, the synthetic application of vinyl radicals to intermolecular carbon–carbon bond formation has remained unexplored in comparison with that of alkyl radicals.[3,4] This is probably because vinyl radicals are so reactive as to easily abstract hydrogen from radical mediators such as Bu_3SnH prior to addition to alkenes. Previously, we have examined the Bu_3SnH-mediated addition of vinyl iodides to electron-deficient alkenes.[3a] The study disclosed that the process via a vinyl radical intermediate is applicable to the stereoselective synthesis of some di- and tri-substituted alkenes while, as predicted, the efficiency of intermolecular addition is not necessarily high due to hydrogen abstraction of the radical intermediate.

Allylstannanes are effective reagents for stereoselective homolytic allylation of alkyl halides.[5] The advantage of the allylstannane method is that a hydrogen donor is not needed, therefore, intermediate alkyl radicals undergo allylation in high efficiency without hydrogen abstraction. In spite of its utility, however, this method has not been applied to vinyl halides to the best of our knowledge. We report here that allylstannanes bearing an electron-withdrawing group at the β-position realize the efficient and, in some cases, stereoselective allylation of vinyl iodides.

Allylation of (*E*)-1-iodo-1-phenyl-1-hexene (**1a**) was chosen for our initial study (Eq. 1). According to Keck's method,[5a] vinyl iodide **1a** was treated with allyltributylstannane (**2a**, 2 equiv.) and AIBN (0.15 equiv.) at 80°C for 24 h. The reaction provided 1,4-dienes **3a** and **4a** in only 5% total yield (**3a**:**4a** 86:14) along with hydrodeiodinated product **5** (4%). Vinyl iodide **1a** was recovered in 61% yield. On the other hand, the use of allylstannane **2b** activated by an electron-withdrawing group raised the yield of adducts (72%, **3b**:**4b** 85:15) under the same conditions.[6] In this case, by-product **5** was not obtained at all.

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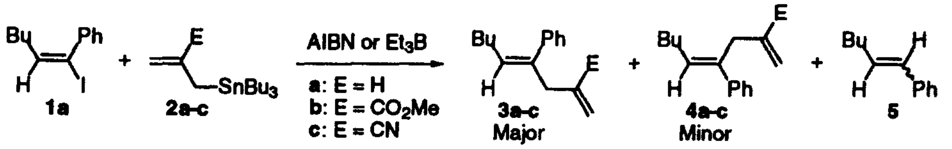
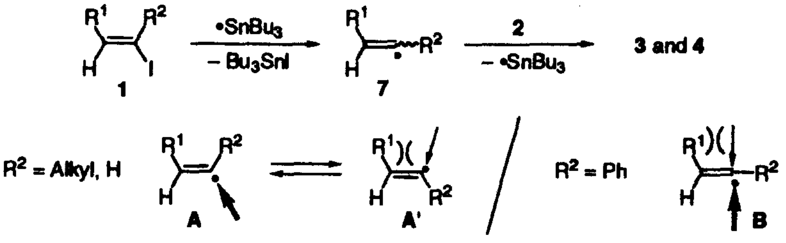
Treatment of **1a** with three equivalents of **2b** gave the adducts in 86% yield. Et_3B–O_2-initiated allylation of **1a** at 25°C exhibited higher stereoselectivity (70%, **3b**:**4b** 92:8).[7] The allylation with allylstannane **2c** bearing a cyano group also proceeded with high stereoselectivity.[6]



(1)

Table 1 delineates the scope of allylation of vinyl iodides with allylstannanes. 1,2-Disubstituted vinyl iodides were transformed into the corresponding 1,4-dienes in better yields than the monosubstituted ones (entries 1–7 vs 8–14). As far as 1,2-disubstituted vinyl iodides are concerned, the present allylation usually exhibited higher efficiency than the Bu_3SnH-mediated reaction previously reported by us.[3a] In most cases, the allylation gave **3** selectively. The substituents R^1 and R^2 of vinyl iodides strongly influenced the stereoselectivity. When R^1 was a bulky group such as *tert*-butyl or dimethylphenylsilyl, high levels of stereoselectivity were achieved (entries 3, 4, 6, 7, and 12). In the case when R^2 was a phenyl group, the allylation showed high stereoselectivity even in the presence of a less bulky substituent as R^1 (entries 1 and 2). The use of *E*- and *Z*-isomers of **1f** led to the same isomeric ratio of allylated products (entries 9 and 10).

The present allylation would proceed via vinyl radicals **7** generated from vinyl iodides **1** by the action of a tributylstannyl radical (Scheme 1). When R^1 is a bulky group, allylstannane **2** should attack the radical center from the opposite site to R^1 to avoid steric repulsion, therefore, 1,4-diene **3** is formed predominantly.[8] The increase in stereoselectivity by a phenyl group as R^2 is attributable to the linear structure of vinyl radical **7a** (R^1=Bu, R^2=Ph), which forces a perpendicular attack of **2** to the radical center.[9] In this situation, the attack to the linear radical **B** from the *syn* side to R^1 would cause more severe steric repulsion than that to the bent radical **A'**.

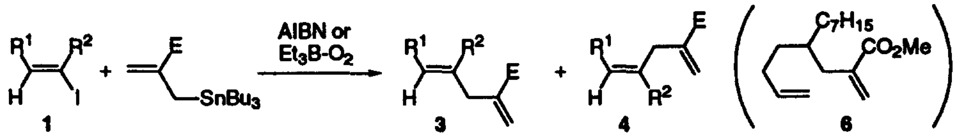


Scheme 1.

In entry 8, 1,7-diene **6** was obtained in a small quantity along with 1,4-dienes **3** and **4**. This would be formed via 1,5-hydrogen transfer of vinyl radical intermediate **7e** (Scheme 2).[10,11] When the reaction of **1e** (0.5 mmol) was performed with a half amount of **2b** (0.75 mmol) in a fivefold amount of benzene (5 mL), the ratio of **6** to **3** and **4** rose to ca. 1:2 (52% total yield). The increased ratio of **6** at a low concentration of **2b** can be rationalized by the deceleration of intermolecular allylation competing with 1,5-hydrogen transfer.

In conclusion, the homolytic allylation of vinyl iodides with certain allylstannanes afforded di- and tri-substituted alkenes in moderate to good yields with high levels of stereoselectivity in some cases. The present study has demonstrated the value of intermolecular addition of vinyl radical for organic synthesis.

Table 1
Homolytic allylation of vinyl iodides with allylstannanes[a]



Entry	Vinyl Iodide	R^1	R^2	Allyl-stannane	AIBN, 80 °C Time / h	AIBN, 80 °C Yield / %	AIBN, 80 °C 3 : 4[b]	Et_3B, 25 °C Time / h	Et_3B, 25 °C Yield / %	Et_3B, 25 °C 3 : 4[b]
1	1a	Bu	Ph	2b	4	86	87:13	24	70	92:8
2	1a			2c	1	70	89:11	24	57	91:9
3	1b	t-Bu	Ph	2b	1	76	>99:1	24	83	>99:1
4	1b			2c	1	72	>99:1	24	66	>99:1
5	1c	C_5H_{11}	C_5H_{11}	2b	1	76	52:48[c]	24	77	53:47[c]
6	1d	t-Bu	Bu	2b	1	71	93:7	2	78	94:6
7	1d			2c	1	63	92:8	24	48	94:6
8	1e	$C_{10}H_{21}$	H	2b	1	34 (4)[d]	57:43	3	55 (1)[d]	56:44
9	1f	PhCH(OH)	H	2b	1	59	69:31	6	40	67:33
10	1f[e]			2b	1	52	68:32	6	40	67:33
11	1g	PhCH(OR) R=TBDMS	H	2b	1	57	77:23	6	58	74:26
12	1h	$PhMe_2Si$	H	2b	1	65[f]	98:2	5	60	>99:1
13	1i	H	$C_{10}H_{21}$	2b	2	60	-	-	-	-
14	1i			2c	2	53	-	-	-	-

[a] All reactions were performed with 0.50 mmol of an (*E*)-vinyl iodide, 1.5 mmol of an allylstannane, and 0.05 mmol of AIBN or Et_3B (1 M in hexane) in benzene (1 mL) at 80 °C or 25 °C unless otherwise noted. In the Et_3B-initiated reaction, air (10 mL) was bubbled through the benzene solution with a syringe after addition of Et_3B.

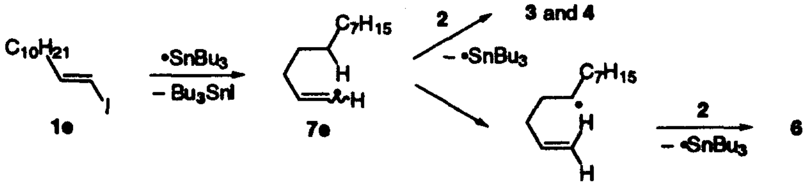
[b] The stereochemistry and ratio were determined by ^1H NMR analysis.

[c] The stereochemistry was not determined.

[d] The value in parentheses is the yield of **6**.

[e] Z-Isomer of **1f** was used as a vinyl iodide.

[f] An increased amount of benzene (5 mL) was used.



Scheme 2.

Acknowledgements

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