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Catalytic Use of Organostannyl Radical: The Reaction of 1,2,3-Selenadiazole with Olefins in the Presence of a Catalytic Amount of Tributyltin Hydride

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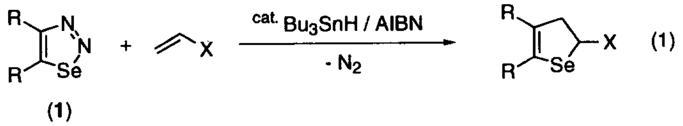
Abstract: When 1,2,3-selenadiazoles were treated with an excess amount of olefins in the presence of a catalytic amount of Bu_3SnH and AIBN, the addition of a vinyl radical, which was generated *in situ* by the denitrogenation of 1,2,3-selenadiazoles, to the carbon-carbon double bond followed by intramolecular cyclization proceeded efficiently to afford the corresponding dihydroselenophenes in moderate to good yields.

The free radical reaction is a popular and important reaction in organic synthesis.[1] In particular, radical-mediated reactions employing a stoichiometric or excess amount of an organotin compound such as tributyltin hydride or allyltributyltin have recently become a useful tool in organic synthesis.[2] In these stannyl radical-mediated reaction pathways, organostannyl radicals generated *in situ* were converted into organotin compounds having stable Sn-X bonds (X = halogen or heteroatom function) *via* the abstraction of the halogen atom or heteroatom function from R-X by the stannyl radical. There are only a few reports on the catalytic use of organotin compounds due to the difficulty in the regeneration of an organostannyl radical from the very stable organotin intermediate.[3,4]

Recently, tributyltin hydride (Bu_3SnH)-mediated reactions in the presence of a stoichiometric or excess amount of metal hydride and a small amount of a radical initiator have been reported: (1) dehalogenation of organic halides,[5] (2) reduction of azides,[6] (3) reduction of α,β-unsaturated ketones,[7] (4) deoxygenation of alcohols,[8] (5) reductive cyclization of enals and enones,[9] and (6) conversion of nitroalkanes to alkanes.[10] However, these transformations require the use of a stoichiometric or excess amount of a second metal hydride capable of regenerating Bu_3SnH.[11] We have now found that a catalytic amount of the tributylstannyl radical generated *in situ* from tributyltin hydride/AIBN or allyltributyltin/AIBN markedly promoted the reaction of the 1,2,3-selenadiazoles (**1**) with olefins (Eq. 1).[12]



Treatment of 1,2,3-selenadiazole (**1a**) derived from cyclohexanone with a catalytic amount of Bu_3SnH (0.05 equiv.) and AIBN (0.025 equiv.) in benzene solution (2.5 mL) at 80 °C for 5 h produced the 1,4-diselenin deriva-

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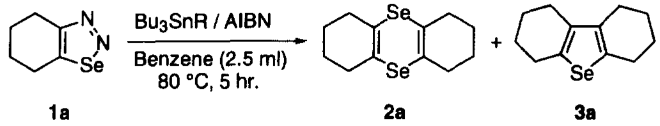
tive (**2a**) in 77 % yield along with a 15 % yield of the selenophene derivative (**3a**) (Entry 1 in Table 1). On the other hand, in the absence of Bu3SnH and AIBN, the reaction was extremely slow and afforded **2a** in 17% yield along with the recovery of the starting selenadiazole (**1a**) (77 %) (Entry 3). When allyltributyltin was employed in place of Bu3SnH, similar reaction smoothly proceeded to afford 1,4-diselenin (**2a**) in 81 % yield (Entry 2). These results show that a catalytic amount of the tributylstannyl radical significantly promoted the denitrogenation of **1a** followed by dimerization giving **2a**.

The reaction pathway in Scheme 1 is proposed to account for these catalytic reactions: (i) radical attack of the tributylstannyl radical derived from a Bu3SnH/AIBN or allyltributyltin/AIBN system on the selenium atom of **1a**, (ii) denitrogenation to form a vinyl radical species (**4a**), (iii) the attack of the vinyl radical (**4a**) on the selenium atom of another molecule of **1a**, (iv) the elimination of the nitrogen molecule, and (v) intramolecular cyclization of the vinyl radical to form 1,4-diselenin (**2a**) and the regeneration of the tributylstannyl radical.

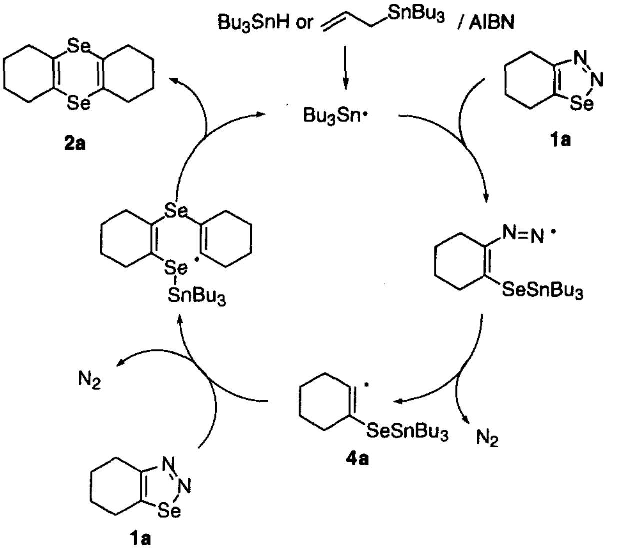
Table 1. Reaction of 1,2,3-Selenadiazole (**1a**) in the Presence of a Catalytic Amount of Organotin Compounds.[a)]



Entry	Bu3SnR / AIBN (mol%)		Yield / %[b)]	
			2a	3a
1	Bu3SnH	(5 / 2.5)	77	15
2	allyl-SnBu3	(5 / 2.5)	81	7
3[c,d)]	None	(0 / 0)	17	2

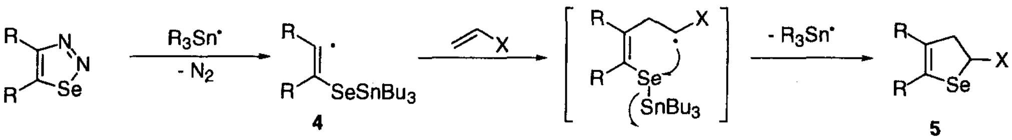
a) Reaction conditions: **1a** (0.5 mmol), Bu3SnR (0.025 mmol), AIBN (0.0125 mmol) and benzene (2.5 mL) at 80 °C for 5 hr.
b) GC yield. c) At 80 °C for 15h. d) **1a** (77 %) was recovered.

Scheme 1. A Plausible Reaction Path



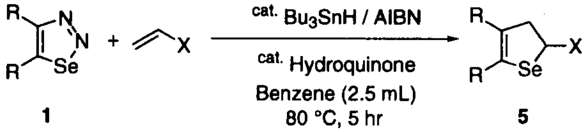
On the basis of the proposed reaction pathway, we examined the synthesis of dihydroselenophene (**5**) by the addition of the vinyl radical species (**4**) to the carbon-carbon unsaturated double bond followed by intramolecular cyclization (Scheme 2). When **1a** was allowed to react with an excess amount of ethyl acrylate (**6a**) (200 equiv.) in the presence of a catalytic amount of Bu3SnH (0.05 equiv.)/AIBN (0.025 equiv.) at 80 °C for 5 h, the corresponding dihydroselenophene (**5a**), the 1:1 addition product between **1a** and **6a**, was formed in 70 % yield along with the recovery of **1a** (17 %) (Entry 1 in Table

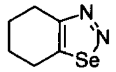
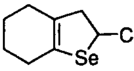
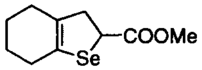
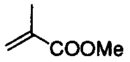
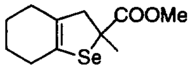
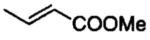
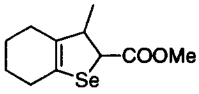
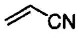
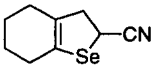
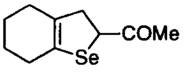
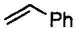
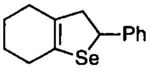
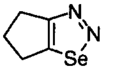
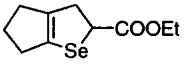
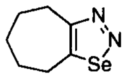
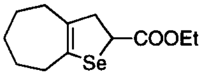
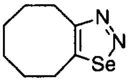
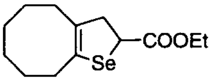
Scheme 2.



2).[13] The yield of **5a** was improved by the addition of a small amount of hydroquinone in order to prevent the oligomerization of **6a** (Entry 2).[14] Table 2 shows the results of the tributylstannyl radical-catalyzed reaction of 1,2,3-selenadiazoles with various olefins. During the reaction of methyl acrylate, acrylonitrile and methyl vinyl ketone, the addition products were also formed in 79 %, 67 % and 74 % yields, respectively (Entries 3, 6 and 7). Methyl methacrylate also gave the corresponding dihydroselenophene in 51 % yield without the influence of the substituent at the α position (Entry 4). In contrast to the reaction with methyl methacrylate, when methyl crotonate, in which the methyl group is substituted at the β-position, was used as an olefin, the addition of vinyl radical species **4** to the carbon-carbon double bond was suppressed and 1,4-diselenin (**2a**) was formed as the main product (Entry 5). In the case of styrene, the addition product was formed in 76 % yield (Entry 8). Furthermore, we examined the reaction of various 1,2,3-selenadiazoles with ethyl acrylate (200 equiv.) using a catalytic amount of Bu_3SnH and AIBN. Similar to cyclohexeno-1,2,3-selenadiazole, the 1,2,3-selenadiazoles derived from cyclopentanone and cycloheptanone gave the corresponding dihydroselenophenes in 66 and 26 % yields, respectively (Entries 9 and 10). In the case of the 1,2,3-selenadiazole derived from

Table 2. Reaction of 1,2,3-Selenadiazole with Olefin in the Presence of a Catalytic Amount of Bu_3SnH and AIBN[a)]



Entry	1,2,3-Selenadiazole	Olefin	Product	Yield / %[b)]
1[c,d)]	 (**1a**)	 (**6a**)	 (**5a**)	70
2	**1a**	**6a**	**5a**	86
3	**1a**			79
4	**1a**			51
5[e)]	**1a**			8
6	**1a**			67
7	**1a**			74
8	**1a**			76
9		(**6a**)		66
10[f)]		(**6a**)		26
11[g)]		(**6a**)		2

a) Reaction conditions: selenadiazole (0.5 mmol), Bu_3SnH (0.025 mmol), AIBN (0.0125 mmol), hydroquinone (0.05 mmol) and benzene (2.5 mL) at 80 °C for 5 hr. b) GC yield. c) In the absence of hydroquinone. d) **1a** (17 %) was recovered. e) **2a** was formed in 75 % yield, predominanatly. f) 1,2,3-Selenadiazole (49 %) was recovered. g) 1,2,3-Selenadiazole (52 %) was recovered.

cyclooctanone, the yield of the addition product was very low (Entry 11).

It is interesting to note that the tributylstannyl radical has excellent catalytic activity for the degradative dimerization and for the reaction of 1,2,3-selenadiazoles with olefins. Further studies on application of the tributylstannyl radical-catalyzed reaction are currently underway.

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11) More recently, R. E. Maleczka, Jr. showed a new approach for the catalytic use of organotin compounds. See: Terstiege, I.; Maleczka, Jr. R. E. *J. Org. Chem.* **1999**, *64*, 342.

12) For reviews of the chemistry of hindered1,2,3-selenadiazoles, see: Ando, W.; Tokitoh, N. *Heteroatom Chem.* **1989**, *2*, 1 and references cited therein.

13) In the absence of benzene, the yield of **5a** was slightly decreased (55 %).

14) We can not explain in detail the reason for the improvement in the yields of addition products in the presence of hydroquinone. However, we suggest that the rates of the attack of the Bu_3Sn radical to 1,2,3-selenadiazole, the addition of the vinyl radical to the carbon-carbon double bond and the intramolecular cyclization were faster than that of the reaction of the tributylstannyl radical with hydroquinone.