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Desulfurizative Stannylation of Allyl Sulfide Using Tributylstannyllithium

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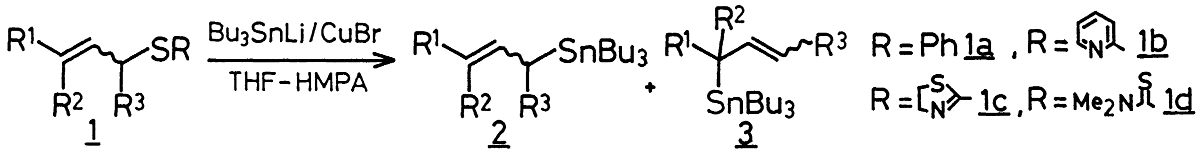
Allylstannanes were prepared by the reaction of allyl sulfides with tributylstannyllithium in the presence of CuBr and HMPA in good yields.

Alkylation of allyl sulfide is an important method for the carbon-carbon bond formation and various highly regioselective reactions were reported.1) However, the regioselectivity of the reductive desulfurization of alkylated allyl sulfides to olefins has yet been insufficient in general as compared with that of the alkylation despite the numerous efforts to develop the reagents for this purpose.1c,d,e,2) One of the most successful methods reported by Ueno and Okawara consists of the desulfurizative stannylation of allyl sulfide and the treatment of the resulting allylstannane with acetic acid or hydrochloric acid.3) This stannylation using tri-n-butyltin hydride and azobisisobutyronitrile, however, is applicable only to the allyl sulfide which has a structure of terminal olefin.

In connection with our study on the reductive metalation of organosulfur compounds utilizing tributylstannylmetal species,4) we investigated the reaction of substituted allyl sulfides with tributylstannyllithium under various reaction conditions. In this communication, we wish to report a versatile method for the transformation of allyl sulfides to allylstannanes as shown in the following scheme.



First we examined the reaction of tributylstannyllithium with substituted allyl phenyl sulfide (1a). When α-monosubstituted allyl sulfide was allowed to react with tributylstannyllithium in the presence of hexamethylphosphoric triamide (HMPA), the S_N2' type reaction preferentially proceeded to give the corresponding allylstannane (3) as a mixture of stereoisomers (run 1). It was found that the yield of 3 was increased by the use of CuBr as an additive (runs 2 and 3). Further it was confirmed that the use of excess tributylstannyllithium was necessary to complete the reaction (runs 4 and 5).

The typical experimental procedure is as follows; to a mixture of 4-phenyl-3-(phenylthio)-1-butene (120 mg, 0.5 mmol) and CuBr (316 mg, 2.2 mmol) in THF

(3 ml)-HMPA (1 ml) was added a solution of tributylstannyllithium5) (2 mmol) in THF (1.8 ml) at 0 °C under argon with stirring. After 3 h, the reaction mixture was quenched by addition of a phosphate buffer solution (pH 7, 20 ml). The organic material was extracted with CH_2Cl_2, dried over Na_2SO_4, and condensed under reduced pressure. The residue was chromatographed on silica gel (hexane) and 1-phenyl-4-(tributylstannyl)-2-butene (175 mg) was isolated in 83% yield.

In a similar manner, various allylstannanes (2 and 3) were prepared by the reaction of substituted allyl phenyl sulfides (1a) (Table 1).

Table 1. Desulfurizative stannylation of allyl phenyl sulfides (1a)a)

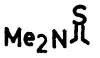
Run	R^1	R^2	R^3	CuBr equiv.	Temp °C	Time h	Product	Yieldb) %
1	H	H	$Ph(CH_2)_2$	—	r.t.	2.5	3	38
2	H	H	$Ph(CH_2)_2$	2.0	0	2	3	78
3	H	H	$Ph(CH_2)_2$	4.4	r.t.	3	3	78
4c)	H	H	$Ph(CH_2)_2$	1.0	0-r.t.	overnight	3	52
5d)	H	H	$Ph(CH_2)_2$	2.0	0-r.t.	overnight	3	71
6e)	H	H	$Ph(CH_2)_2$	4.4	0-r.t.	overnight	3	68
7	H	H	$PhCH_2$	4.4	0	3	3	83
8	H	H	$CH_3(CH_2)_3$	4.0	r.t.	3	3	51
9	H	$Ph(CH_2)_2$	H	—	r.t.	2	2	31
10	H	$Ph(CH_2)_2$	H	2.0	0	3	2	77
11	H	$Ph(CH_2)_2$	H	4.4	0-r.t.	6	2	48
12	H	$PhCH_2$	H	2.0	0	3	2	83
13	H	CH_3	$PhCH_2$	2.0	0	3	2,3f)	83
14	CH_3	CH_3	$Ph(CH_2)_2$	0.05	r.t.	4.5	2	72
15d)	CH_3	CH_3	$Ph(CH_2)_2$	0.1	0-r.t.	overnight	2	67
16	CH_3	CH_3	$PhCH_2$	—	r.t.	2	2	55
17	CH_3	CH_3	$PhCH_2$	0.05	r.t.	2	2	78
18	CH_3	CH_3	CH_3	0.1	r.t.	overnight	2	56

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) 1.0 equiv. of Bu_3SnLi was used. d) 2.0 equiv. of Bu_3SnLi were used. e) In the absence of HMPA. f) 2:3 = 53:47.

The results listed in Table 1 indicate that the optimal amount of CuBr varies with the structures of allyl sulfides. In all cases examined, the present desurfurizative stannylation proceeded with excellent regioselectivity except for the reaction of α,γ-disubstituted allyl phenyl sulfide. When the mono or trisubstituted allyl sulfide was employed, tributylstannyl group is introduced to the less substituted side of an allylic system regardless of the original location of phenylthio group. Although it is uncertain at present whether the reaction is kinetically or thermodynamically controlled,[6] it is assumed that the high regioselectivity of the present reaction is attributed to the bulkiness of tributylstannyl group. On the other hand, no selectivity exists in the reaction of allyl phenyl sulfide possessing two secondary centers at the both end of allylic system.

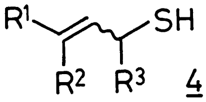
It is well known that the α/γ ratio of the alkylation of allyl sulfide is increased by the replacement of phenyl group of phenyl sulfide with a nitrogen containing substituent.[1c,d,e] Then the desulfurizative stannylation of allyl 2-pyridyl and 2-thiazolyl sulfides (1b and 1c) and allyl dithiocarbamates (1d) was examined (Table 2). In the reaction of allyl 2-pyridyl and 2-thiazolyl sulfides (1b and 1c), the corresponding allylstannanes (2 and 3) were obtained in good yields. The decrease of the yield, however, was observed when the highly substituted allyl sulfide was employed (runs 5 and 11). Contrary to the above results, the treatment of S-crotyl dithiocarbamate with tributylstannyllithium in the presence of CuBr gave the corresponding allylic thiol (4) as a main product (run 14). The formation

Table 2. Desulfurizative stannylation of allyl 2-pyridyl sulfides (1b), allyl 2-thiazolyl sulfides (1c), and allyl dithiocarbamates (1d)[a]

Run	R	R^1	R^2	R^3	CuBr equiv.	Additive	Time h	Product	Yield[b] %
1[c]		H	H	PhCH$_2$	2.0	HMPA[e]	3	3	78
2[c]		H	H	Ph(CH$_2$)$_2$	2.0	HMPA[e]	3	3	75
3		H	PhCH$_2$	H	2.0	HMPA[f]	4.3	2	54
4		CH$_3$	H	PhCH$_2$	2.0	LiBr[g]	1	2,3[h]	70
5[d]		CH$_3$	CH$_3$	PhCH$_2$	2.0	LiBr[g]	22.5	2	38
6		H	H	PhCH$_2$	0.1	HMPA[e]	1	3	73
7		H	H	CH$_3$(CH$_2$)$_3$	0.1	HMPA[e]	1	3	72
8		H	PhCH$_2$	H	2.0	HMPA[e]	0.5	2	88
9		CH$_3$	H	PhCH$_2$	2.0	LiBr[g]	1	2,3[i]	53
10		CH$_3$	CH$_3$	PhCH$_2$	0.1	HMPA[e]	1	—	0 (89[j])
11		CH$_3$	CH$_3$	PhCH$_2$	2.0	LiBr[g]	1.3	2	53
12		H	H	PhCH$_2$	2.0	HMPA[e]	2	3	52
13[c]		H	H	Ph(CH$_2$)$_2$	2.0	HMPA[e]	4	3	50
14		CH$_3$	H	Ph(CH$_2$)$_2$	2.0	LiBr[g]	0.5	—	trace (54[j])

[a] All the reactions were carried out at 0 °C with a similar procedure as described in the text, unless otherwise noted. [b] All compounds gave satisfactory spectral data. [c] 2.0 equiv. of Bu$_3$SnLi were used. [d] Bu$_3$SnLi was added at 0 °C and the reaction mixture was warmed up to r.t. [e] 2 ml per 1 mmol of 1. [f] 4 ml per 1 mmol of 1b. [g] 2.0 equiv. [h] 2:3 = 45:55. [i] 2:3 = 54:46. [j] The yield of the allylic thiol (4).

of 4 was also observed in the reaction of prenyl 2-thiazolyl sulfide carried out in the presence of a catalytic amount of CuBr (run 10). As shown in Table 2, the tendency to form the allylstannane which has a tributylstannyl group at the less substituted side of an allylic system was also found in these reactions.



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Since allylstannanes are useful reagents for allylation of various organic compounds,7) it is noted that the present reaction not only provides a convenient method for the transformation of allyl sulfides to olefins but also extends the applicability of allyl sulfides in organic synthesis.

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References

1) For example: a) J. F. Biellmann and J. B. Duccep, Tetrahedron Lett., 1969, 3707; b) K. Kondo and M. Matsumoto, ibid., 1976, 391; c) K. Narasaka, M. Hayashi, and T. Mukaiyama, Chem. Lett., 1972, 259; d) K. Hirai, H. Matsuda, and Y. Kishida, Tetrahedron Lett., 1971, 4359; e) T. Nakai, H. Shiono, and M. Okawara, Chem. Lett., 1975, 249.

2) K. Hirai and Y. Kishida, Tetrahedron Lett., 1972, 2743; R. O. Hutchins and K. Learn, J. Org. Chem., 47, 4380 (1982).

3) Y. Ueno and M. Okawara, J. Am. Chem. Soc., 101, 1893 (1979); Y. Ueno, S. Aoki, and M. Okawara, ibid., 101, 5414 (1979).

4) T. Takeda, K. Ando, A. Mamada, and T. Fujiwara, Chem Lett., 1985, 1149; T. Takeda, H. Oshima, M. Inoue, A. Togo, and T. Fujiwara, ibid., 1987, 1345.

5) The THF solution of tributylstannyllithium was prepared by the method reported by Tamborski et al.a) and the concentration was determined by the reaction with 2-cyclohexenone.b) a) C. Tamborski, F. E. Ford, and E. J. Soloski, J. Org. Chem., 28, 237 (1963); b) W. C. Still, J. Am. Chem. Soc., 99, 4836 (1977).

6) Fleming and Rowley noted the possibility of the 1,3 allylic shift of tributylstannyl group of some secondary allylstannanes; I. Fleming and M. Rowley, Tetrahedron Lett., 27, 5417 (1986).

7) For example: M. Kosugi, K. Sasazawa, Y. Shimizu, and T. Migita, Chem. Lett., 1977, 301; M. Kosugi, Y. Shimizu, and T. Migita, J. Organomet. Chem., 129, C36 (1977); A. Hosomi, H. Iguchi, M. Endo, and H. Sakurai, Chem. Lett., 1979, 977; B. M. Trost and E. Keinan, Tetrahedron Lett., 21, 2595 (1980); Y. Yamamoto, H. Yatagai, Y. Naruta, and K. Maruyama, J. Am. Chem. Soc., 102, 7108 (1980); W. J. Scott, G. T. Crisp, and J. K. Stille, ibid., 106, 4630 (1984); B. M. Trost and T. Sato, ibid., 107, 719 (1985).

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