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A NOVEL HOMOLYTIC SUBSTITUTION ON VINYLIC CARBON. A NEW ROUTE TO VINYL STANNANE

Yoshihiko Watanabe*, Yoshio Ueno, Takumi Araki, Takeshi Endo and Makoto Okawara

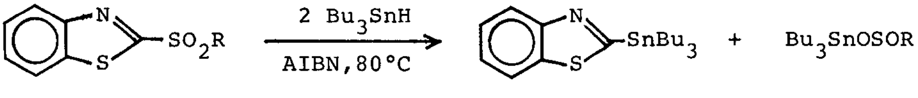
Research Labolatory of Resources Utilization, Tokyo institute of Technology,
Nagatsuta, Midoriku, Yokohama 227

Abstract: 2-(Alkylsulfonyl)benzothiazole 1 reacted with tributyltin hydride in the presence of azobisisobutyronitrile at 80°C to give 2-(tributylstannyl)benzothiazole in 67-79% yield. Similarly, vinylsulfone 4 gave the corresponding vinylstannane in 58-78% yield.

Organometallic reagents have been widely used in organic synthesis.[1] A serious limitation of such reagents, however, is steric hindrance of big metal atoms. For example, homolytic hydrostannylation generally proceeds smoothly in the case of terminal olefines but not internal ones.[2] This type of problem seems to be observed in other big metals including transition ones.[3]

In this communication, we report a new type of homolytic substitution on vinylic carbon atom. Our approach is based on an assumption that initial electron transfer from organometallics to substrates followed by the metal-carbon bond formation may greatly overcome the steric factors, as well mentioned in S_{RN} reaction of nitro compounds.[4]

In order to visualize our idea, we attempted the reaction of electron deficient compounds containing good leaving group, with tributyltin hydride. Thus, we found that 2-(alkylsulfonyl)benzothiazole 1 reacted with two equivalents of tributyltin hydride in the presence of catalytic amount of azobisisobutyronitrile (AIBN, 2mol%) in refluxing benzene for 0.5-2 h to afford 2-(tributylstannyl)benzothiazole 2 (Table 1).



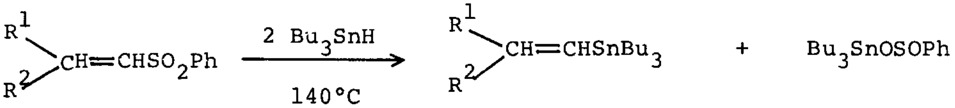
1 2 3

Table 1. Reaction of 2-(alkylsulfonyl)benzothiazole 1 with tributyltin hydride

Substrate	R	Reaction time	Yield of 2	Yield of 3
1a	$CH_3(CH_2)_{15}$	2 h	79 %	89 %
1b	$PhCH_2CH_2$	1 h	67 %	90 %
1c	CH_3COCH_2	0.5 h	72 %	0 %

The sulfonyl group was trapped with tributyltin hydride yielding tributylstannylsulfinate 3. The products were isolated by the fractional distillation.[5] Acetonyl sulfone 1c, however, was stannylated without formation stannylsulfinate 3c under equimolar condition.[6]

Furthermore, this type of reaction was extended to more simple substrates, i.e., vinylsulfone 4. As expected, 4 reacted with two equivalents of tributyltin hydride in refluxing xylene to afford vinylstannane 5.[7]



4 5 6

Table 2. Reaction of vinylsulfone with tributyltin hydride

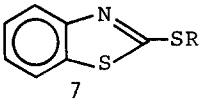
Substrate	R^1	R^2	Reaction time	yield* of 5	Yield* of 6
4a	H	C_6H_5	7 h	75 %	85 %
4b	H	$p\text{-}ClC_6H_4$	8 h	78 %	86 %
4c	H	$p\text{-}CH_3OC_6H_4$	8 h	65 %	85 %
4d	H	2-furyl	8 h	72 %	83 %
4e	CH_3	CH_3	24 h	58 %	75 %

*isolated yield by Kugelrohr

Similarly, furan-substituted vinylstannane 5d was obtained in 72% yield from the corresponding sulfone 4d. However, alkyl-substituted vinylstannane 5e was obtained in slightly low yield (58%) even for 24 h reaction time.

The present reaction offers an example of homolytic substitution on vinylic carbon, which has hitherto been reported in very few cases in contrast to the homolytic aromatic substitution. Vinylstannanes are synthetically interesting substrates in palladium chemistry[8], and also precursors for ethinylic or vinylic compounds such as vinyllithiums[9]. In addition, a potential reactivity of vinylic stannane 2 is highly expected. In fact, tributylstannyl group in 2 is very reactive, since 2 is quantitatively destannylated to benzothiazole 7 on chromatography (alumina or silicagel-methanol).

The less electron deficient 2-(alkylthio)benzothiazoles 7 exhibit completely different behavior towards tributyltin hydride under the similar conditions.

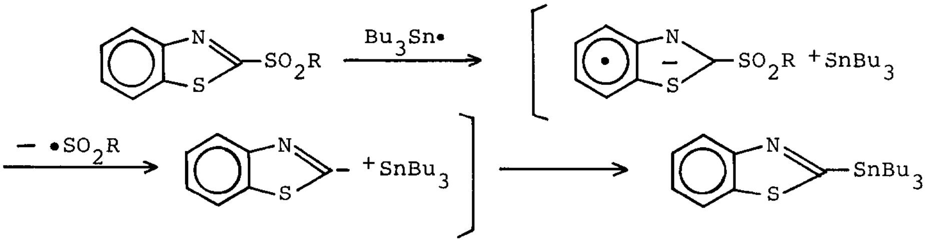


7

7a R=CH_3
7b R=p-$ClC_6H_4CH_2$
8 R=Bu_3Sn

Although 2-(methylthio)benzothiazole 7a was recovered, p-chlorobenzyl derivative 7b gave 2-(tributylstannylthio)benzothiazole 8 in 97% yield.

Although addition-elimination mechanism can not be excluded completely, a plausible mechanism for the present stannylation reaction may involve electron transfer from tributyltin radical to sulfone. Thus, tributyltin hydride reacts with a certain azomethine group at carbon but not nitrogen[10].



Moreover, Tieco et al. have suggested the similar electron transfer mechanism for the reaction of 2-(phenylsulfonyl)benzothiazole with nucleophilic adamantyl radical[11].

In summary, although further study is necessary for definitive mechanism,[12] the present findings offer a new entry to overcome the steric factor in carbon-tin bond formation between a bulky tin atom and a sterically hindered internal carbon atom.

References and notes

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5. In all cases, a small amount of benzothiazole was isolated in 5-10% yield. All new compounds showed satisfactory physical and spectral data.

6. The eliminated sulfonyl radical ($\cdot SO_2CH_2COCH_3$) may cleave to sulfur dioxide and acetonyl radical prior to the formation of stannylsulfinate ($Bu_3SnOSOCH_2COCH_3$). Acetonyl radical may give eventually acetone.
7. The stereochemistry of 5a was estimated by ^1H NMR. The trans isomer (98%) was formed predominantly. See, A.J.Leusick, H.A.Budding, J.W.Marsman, J. Organometal. Chem., 9, 285 (1967).
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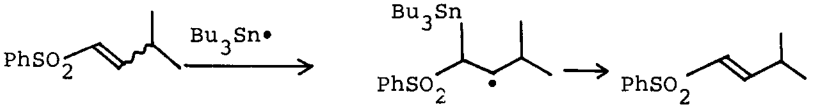
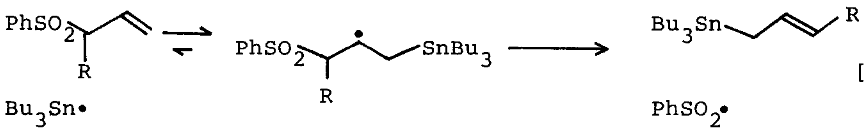
11. M.Fiorentino, L.Testaferri, M.Tiecco, L.Troisi, J. Chem. Soc., Chem. Comm., 316 (1977).
12. M.Julia et al. reported the tributyltin hydride catalyzed cis-trans isomerization of vinylsulfone, although they can not obtain substituted products described here. M.Julia, C.Rolando, J.N.Verpeaux, Tetrahedron Lett., 23, 4319 (1982). Their postulation (addition and elimination of tin radical, eq 1) seems to be unlikely, since we have already confirmed the exclusive splitting of sulfonyl radical but not tin one in a closely related system (eq 2). (Y.Ueno, S.Aoki, M.Okawara, J. Am. Chem. Soc., 101, 5414 (1979)). Julia's result can be explained by the partial electron transfer leading to the intermediate similar to the anion-radical tin-cation complex.



[1]



[2]

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