Tributyl[2-(trimethylsilyl)prop-2-enyl]stannane: A Highly Efficient Reagent for the Allylation of Radicals

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Abstract. Allylation rates of radicals with tributyl[2-(trimethylsilyl)prop-2-enyl]stannane (2) have been compared with the ones of the (prop-2-enyl)stannane (3) and [2-(methyl)prop-2-enyl]stannane (4). The Me, Si substituent showed a rate-accelerating effect (4.2:1 to 6.5:1) relative to the H-atom and the Me group for nucleophilic radicals. With electrophilic radicals, the Me group has a better rate accelerating effect than the Me3Si group. All these results can be understood by postulating a partially polarized transition state. The 1-substituted vinylsilanes which are produced by radical allylation with 2 have been converted by protodesilylation and ozonolysis to alkenes and α-hydroxy ketones.

Allylstannanes have been introduced by Keck et al. [1] for very efficient C–C bond formation via radical additions. The fragmentation mechanism involved in these reactions allows to conduct Sn-radical based chains without using Bu3SnH. Consequently, unwanted direct reduction of the radical intermediates is suppressed.

It was recently shown that the efficiency of these reactions is also due to the fact that allylstannanes are more reactive than simple alkenes toward radicals by at least one order of magnitude [2]. In connection with our work on nucleophilic and electrophilic radicals, we have faced situations where radical additions to (prop-2-enyl)stannane were not efficient because of competing radical processes such as dimerization, disproportionation, and H-atom abstraction from the solvent. This prompted us to search for a more reactive synthetic equivalent of (prop-2-enyl)stannane. Recently, Lee et al. [3] have reported that radical allylation reactions with [2-(trimethylsilyl)prop-2-enyl]triphenylstannane were apparently faster and higher yielding than reactions with the non-substituted (prop-2-enyl)stannane [4]. To find out the origin of this efficiency, we decided to investigate the allylation reaction of several radicals with the 2-silylated allylstannane 2 and to compare the allylation rates with the non-substituted and the 2-methyl-substituted allylstannanes 3 and 4, respectively (Scheme 1). Moreover, we also report some typical and synthetically useful one-step transformations of the substituted vinylsilanes 5a–e, which are obtained from the radical allylations with 2.

The substituted allylstannane 2 was prepared according to Schlosser’s procedure [5] in 50% yield by metallation of 2-(trimethylsilyl)prop-1-ene with BuLi/t-BuOK and subsequent reaction with Bu3SnCl. This one-pot procedure was found to be faster and more convenient than the ones of Lee et al. [3] and Overman and coworkers [6]. The reactivity of 2 toward radicals was then examined by competition experiments with tributyl(2-enyl)stannane (3) and tributyl[(2-methyl)prop-2-enyl]stannane (4). In a typical experiment, the radical precursor R= X (0.25 mmol) was irradiated for 12 h in benzene at 10° in the presence of

Table. Competition Experiments for the Allylation of 1a–e with the Allylstannanes 2–4 and Allylation Yields with 2

| Entry | R–X | 5/6 (%) | 5/7 (%) | Yield (5) (%) |
|-------|-----|--------|--------|--------------|
| 1     | 1a  | 4.2:1  | 4.4:1  | 40           |
| 2     | 1b  | 5:1    | 6:5:1  | 63           |
| 3     | 1c  | 2.6:1  | 1.2:1  | 75           |
| 4     | 1d  | 3.2:1  | 1:1.8  | 63           |
| 5     | 1e  | 3:1    | 1:2.5  | 80           |

a) From 1 (0.25 mmol), 2 (1 mmol), 3 (1 mmol) and AIBN (10 mg) in benzene (4 ml).

b) From 1 (0.25 mmol), 2 (1 mmol), 4 (1 mmol) and AIBN (10 mg) in benzene (4 ml).

c) From 1 (5 mmol), 2 (6 mmol) and AIBN in benzene (15 ml).
AIBN and an equimolar mixture of 2/3 or 2/4 (1 mmol of each stannane). The product ratio was then determined by H-NMR, and the results are summarized in the Table. With the alkyl radical generated from 1a, the silylated stannane 2 reacted ca. four times faster than the H- and the Me-substituted (propenyl)stannanes 3 and 4. The MeO-substituted alkyl radical derived from the O,S acetate 1b showed an even stronger Me,Si-induced rate enhancement (5b/6b 5:1 and 5b/7b 6.5:1). With the sulfynylated radical 1e, the rate enhancement was less pronounced relative to the (prop-2-enyl)stannane 3 (5e/6c 2.6:1). Almost no rate enhancement was observed relative to the methylated reagent 4 (5e/7c 1.2:1). In case of the electrophilic sulfonyl substituted radical 1d, the Me,Si group had an activating effect relative to H (5d/6d 3.2:1), but the Me-substituted allylstannane 4 was more effective (5d/7d 1:1.8). A very similar picture was observed with the malonyl radical 1c which reacted faster with 2 than with 3 (5e/6e 3:1), but the reaction with 4 was even faster (5e/7e 1:2.5). We also checked that the rate enhancement led to better yields of isolated products. For example, the allylation of 1b with 2 gave 5b in 63% yield (Entry 2), although the reaction with 3 gave 6b in less than 5% yield [7]. Good yields have also been obtained with electrophilic radicals as illustrated by the conversion of 1d and 1e to 5d and 5e in 63% and 80% yield, respectively (Entries 4 and 5).

Our results are neither properly explained by orbital considerations [8] nor by stabilization of the radical adducts A–C (Fig.9) [9]. However, polarization of the transition state offers a satisfactory explanation. The addition of nucleophilic radicals (Entries 1 and 2) causes a polarization of the transition state as indicated in the Figure (D–F). The Me,Si substituent stabilizes the partial negative charge in the transition state D. Such a stabilization is not present in transition states E and F. A similar explanation based on the ability of Si to stabilize adjacent electron-rich centers was proposed to account for the reactivity of α-halosilanes during the reduction with Bu,SnH [10]. With nucleophilic radicals (Entries 4 and 5), the polarization is opposite and a partial positive charge appears at C(2) of the prop-2-enyl group (G–I). The results are coherent with the order of carbocation stabilizing effect. Indeed, it has been shown that a Me group (I) is more stabilizing than a Me,Si group (G), and that a H-atom (H) is less stabilizing [11]. The sulfynylated radical derived from 1c behaves like an ambiphilic radical, and the transition state should not be significantly polarized.

The Me,Si-substituted olefins produced are very useful building blocks [12]. For instance, they can be converted to alkynyl halides [13], methyl ketones [14], (phenylthio)methyl ketones [15], hydroxyketones [16] and alkenes [17]. We have decided to examine the allylation of glucopyranosyl bromide tetraacetate (11; Scheme 3) [19]. Irradiation with a 300-W sunlamp of a solution of 11 and 2 in the presence of AIBN yielded 12 in 70% (α/β 5:1). Ozonolysis of 12 (O3, Me,Si) gave, after chromatography, the diastereoisomERICally pure hydroxyketone 13 in 72% yield. This reaction sequence allows to add three C-atoms containing two oxygenated functionalities and is potentially interesting for chain elongation of carbohydrates [20]. In conclusion, the presence of a Me,Si group on a C=C bond enhances particular-
ly well its reactivity toward nucleophilic radicals. This effect, caused by some degree of polarization of the transition state, can probably be used with other types of olefins in order to make them more suitable for radical reactions. Work in that direction is currently underway in our laboratory.

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Experimental Part

General. THF was freshly distilled from K under Na, CH2Cl2 was distilled from P2O5. Benzene was distilled from CaH2 under N2. For flash column chromatography (FC) and filtration, Merck silica gel 60 (70-230 mesh) was used. TLC column chromatography (FC) and filtration, catechol, spectra were recorded in CDCl3 and chemically corrected) were determined by using a Bruker AC-250 FTIR spectrometer. GC (packed column, SE-54).

General Procedure 1: Radical Allylation with 2. A soln. containing the radical precursor (5 mmol), the stannane (2.42 g, 6 mmol) and AIBN (15 mg) in mg CH2Cl2 (15 ml) was irradiated at 10° for a 300-W sunlamp. Further portions of AIBN (15 mg) were added every 8 h, and the reaction was followed by TLC. Total disappearance of the starting material took between 12 and 36 h. The solvent was then evaporated and the residue purified by FC (hexane, hexane/AcOEt). When an aldehyde was used as radical initiator (1a, 1d, and 1e), MeOH (30 ml) was added after the irradiation period followed by KF (1.5 g), and the mixture was stirred for 1 h and filtered. The filtrate was evaporated and the residue treated as above.

General Procedure 2: Ozonolysis of Vinylsilanes [16]. O3 was passed through a soln. of the vinylsilane (1 mmol) in 10 ml of CH2Cl2 at 78° until persistence of a blue color. The soln. was flushed with N2 until disappearance of the blue color and dimethyl sulfide (0.3 ml, 4 mmol) was added, and the reaction mixture was allowed to warm up to r.t. Evaporation of the solvent gave the crude hydroxymethyl ketone.

Tributyl(2-trimethylsilyl)prop-2-enylstannane [2] (5). A soln. of 2-(trimethylsilyl)prop-1-ene (10.0 g, 175 mmol) in THF (600 ml) was treated at 78° with a 1.6 m BuLi soln. in hexane (121 ml, 192 mmol) followed by a 1.56 M BuOK soln. in THF (112 ml, 175 mmol). The mixture was stirred at -40° for 1.5 h, cooled down to -78°, and transferred via a Teflon cannula (2-3 mm internal diameter) portion to a soln. of Bu2SnCl (57.0 g, 175 mmol) in THF (1 l). After 15 min at 15°, the mixture was poured into brine (2 l) and extracted 3 times with petroleum ether (4, 2, 2). The combined org. phases were dried (MgSO4) and evaporated. FC (AcOEt/hexane 1:4) of the crude product gave 5a (378 mg, 40%). Colorless liquid. 1H-NMR (200 MHz): 5.55 (m, CH2=CH2; J = 3.0, CH2=CHSe; J = 4.5, O=CH-CH=); 5.10 (d, J = 11.6, 6.2, 2.0, CH2=CH2); 2.22-1.90 (m, 24 H); 1.70-1.40 (m, 4 H); 1.32 (d, J = 13.0, 6.7, 1.3, 1.0, O=CH-CH=); 1.08 (t, J = 6.0, OCH3); 2.42 (dd, J = 14.2, 6.7, 1.3, 1.0, CH2=CH-Se; 2.23 (dd, J = 14.2, 6.1, 1.3, 0.8, CH2=CH-Se; 1.12 (s, SeCH2). Anal. calcd. for C15H30OSe: C 57.79, H 5.97. Found: C 57.90, H 5.87.

Methyl 2-Phenyl-1-(phenylselenyl)ethyl Ether (1b). Diphenylsilanediene (1.56 g, 5 mmol) in toluene (5 l) was added to a 1.0 m soln. of DIBAL-H in hexane (10 ml, 10 mmol). The mixture was stirred at r.t. for 30 min, 2-phenylpropanaldehyde dimethyl acetal (0.83 ml, 5.0 mmol) was added and the mixture heated at 50° for 3 h. The cooled reaction mixture was treated with a 5% NaF soln. (17 ml) and extracted with CH2Cl2. Drying (MgSO4), evaporation of the solvent, and FC (EtO/hexane 1:10) of the residue gave 1b (1.10 g, 75%). Yellow liquid. 1H-NMR (200 MHz): 7.70-7.60 (m, 2 arom. H); 7.40-7.20 (m, 3 arom. H); 5.15 (dd, J = 7.0, 5.9, CH(O=Se)(Ph); 3.50 (t, J = 5.9, CHFPh); 3.29 (d, J = 7.0, CH2Ph). 13C-NMR (50.3 MHz): 132.22, 135.49, 129.27, 128.84; 128.17; 127.60; 124.47; 90.33; 57.28; 44.03. Anal. calc. for C24H16OSe (291.25): C 61.86, H 5.44; found: C 61.55, H 5.46.

Phenyl(vinylselenyl)methyl Sulfoxide (1c). A 0.6 m soln. of LiHMDS (108 ml, 65 mmol) in hexane/THF (1:1) was added to 1c (1.02 g) of the crude product gave 1c (295.26): C 52.88, H 4.10; found: C 52.59, H 4.30.

Scheme 3

![Scheme 3](attachment:image1.png)

2,4-(Trimethylsilyl)but-5-en-1-yl, 1,3-dioxyane (5a). From 1a (500 mg, 2.56 mmol) and 2 (1.34 g, 3.3 mmol) according to General Procedure 1.

Conclusion Experiment. A soln. containing the radical precursor 1 (0.25 mmol), AIBN (10 mg), the stannane 2 (403 mg, 1 mmol) and either the stannane 3 (331 mg, 1 mmol) or 4 (345 mg, 1 mmol) in benzene (4 ml) was irradiated at 10° for 12 h with a 300-W sunlamp. The solvent was evaporated and the residue filtered through silica gel (hexane, hexane/AcOEt) to eliminate the tin derivatives. When a halide was used as radical initiator (1a, 1d, and 1e), MeOH (6 ml) was added after the irradiation period followed by KF (300 mg) and the mixture was stirred for 1 h and filtered. The filtrate was evaporated and the solid residue was extracted with CH2Cl2, filtered through cotton, and the filtrate was concentrated before rapid filtration through silica gel as described above. The ratio 5/6 or 5/7 was deduced from 1H-NMR spectra (olefinic protons) and confirmed by GC (packed column, SE-54).

General Procedure 1: Radical Allylation with 2. A soln. containing the radical precursor 1 (5 mmol), the stannane 2 (2.42 g, 6 mmol) and AIBN (15 mg) in CH2Cl2 (15 ml) was irradiated at 10° with a 300-W sunlamp. Further portions of AIBN (15 mg) were added every 8 h, and the reaction was followed by TLC. Total disappearance of the starting material took between 12 and 36 h. The solvent was then evaporated and the residue purified by FC (hexane, hexane/AcOEt). When an aldehyde was used as radical initiator (1a, 1d, and 1e), MeOH (30 ml) was added after the irradiation period followed by KF (1.5 g), and the mixture was stirred for 1 h and filtered. The filtrate was evaporated and the residue treated as above.

General Procedure 2: Ozoneolysis of Vinylsilanes [16]. O3 was passed through a soln. of the vinylsilane (1 mmol) in 10 ml of CH2Cl2 at 78° until persistence of a blue color. The solution was flushed with N2 until disappearance of the blue color and dimethyl sulfide (0.3 ml, 4 mmol) was added, and the reaction mixture was allowed to warm up to r.t. Evaporation of the solvent gave the crude hydroxymethyl ketone.
calc. for C₁₃H₂₄O₅Si (252.45): C 61.85, H 7.99, O 19.57, Si 11.02.

Prop-2-enylltri butylstannane, see ref. [4v] and: S. Abel, T. Linker, B. Giese, Synlett 1991, 171.

Dimethyl (2-Trimethylsilyl)prop-2-en-1-ylvinylpropionate (5e). From 6e (100 mg, 0.7 mmol) and 2 (1.0 g, 6.2 mmol) according to General Procedure 1. FC (AcOEt/hexane 1:1) gave 5e (340 mg, 63%), 1H-NMR (250 MHz): 7.92-7.85 (m, 20 H), 7.73-7.67 (m, 10 H), 7.59-7.50 (m, 30 H), 4.30 (s, OCH₂Si), 3.13 (m, CH₂C₆H₅), 2.49 (s, CH₂C₆H₅), 2.02 (m, CH₂CH₂C₆H₅), 1.90 (m, CH₂CH₂CH₃), 1.80 (m, CH₂CH₂CH₂CH₃), 1.41 (s, CH₃Si), Anal. calc. for C₁₃H₂₀O₂SiSi (444.36): C 54.04, H 7.26, Si 6.23, found: C 54.01, H 7.21, Si 6.23.

1-(α- and β-Glucopyranosyl)-3-hydroxyprop-2-one (13). From 2 (442 mg, 1.0 mmol) according to General Procedure 2. FC (AcOEt/hexane 1:1, AcOEt) gave diastereomerically pure 13 (290 mg, 72%). White solid. M.p. 106-108°H-NMR (250 MHz): 2.57 (s, J = 3.0, CH₃); 4.56 (t, J = 7.0, CH₂(OH)); 4.08 (dd, J = 4.0, 6.0, H-C(1)); 3.83 (dd, J = 10.5, 3.0, H-C(1)); 1.90 (s, CH₃CO); 1.68 (d, J = 7.0, Me); 1.40 (s, Me); 1.30 (s, Me); 1.10 (s, Me). 13C-NMR (62.5 MHz, acetone-CD₃): 170.50 (s, COOCH₃); 146.56 (s, CH₂(OH)); 112.63 (s, C₆H₅); 70.53 (s, CH₂O); 53.82 (s, CH₂O); 45.35 (s, CH₂O); 36.40 (s, CH₂O); 27.40 (s, CH₂O); 23.20 (s, CH₂O). Anal. calc. for C₈H₁₄O₂Si (152.26): C 52.20, H 8.10, Si 8.05, found: C 52.20, H 8.05, Si 8.03.

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