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LETTERS

Synthesis of α-Substituted α,β-Unsaturated Acylsilanes

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Abstract: α-Deprotonation of *tert*-butyldimethylsilyloxy allene is followed by silyl migration from oxygen to carbon. The resulting C-nucleophile adds to aldehydes to generate α,β-unsaturated acylsilanes.

Keywords: *allenes; acyl silanes; rearrangement*

The utility of α,β-unsaturated acylsilanes as building blocks for organic synthesis is well-documented.[1] These materials participate in a number of transformations which are unique to the acylsilane function, including Brook rearrangements,[2] oxidation to carboxylic acids,[3] and fluoride-promoted conversions to ketones and aldehydes.[3] They also react as Michael acceptors with organocuprates,[2a] as well as in $TiCl_4$-promoted allylations[4] and additions of silylated nucleophiles.[5] Unsaturated acylsilanes are Diels-Alder dienophiles,[2a] and they also undergo a variety of [1,3]-dipolar cycloadditions,[6] as well as [3+2] annulations with allenylsilanes,[6] and with ketone enolates.[7] α,β-Unsaturated acylsilanes are usually prepared either by forming the C-C double bond, or by installing the acylsilane functionality in the key step. The C-C double bond has been prepared by means of a Peterson olefination,[3,8] Horner-Wadsworth-Emmons condensation,[9] dehydration[10] or dehydrohalogenation reactions.[11] The acylsilane unit has been prepared by hydrolysis of an α-silyl enol ether,[2a,b; 12] oxidation of an allylic carbinol,[13] silyl cuprate addition to an acyl chloride,[14] enyne hydroboration-oxidation,[15] or by means of the benzotriazole acyl anion methodology.[16] None of these methods is well-suited for the introduction of a functionalized appendage at the α carbon of α,β-unsaturated acylsilanes. Herein we report the generation of a silaacrolein enolate anion, and its addition to aldehydes.

Scheme 1 summarizes our approach. Allene **3** was easily prepared from propargyl alcohol **1** in two steps. *O*-Silylation with *tert*-butyldimethylsilyl chloride gave silyl ether **2** (TBS = *tert*-butyldimethylsilyl),[17] which was isomerized to allene **3** with potassium *tert*-butoxide in 68% overall yield from **1**.[18] This synthesis of **3** is more convenient, and will prove to be more versatile than our earlier approach.[19] α-Deprotonation[20] of **3** with *tert*-butyllithium presumably led to allenyllithium species **4** first. After 30 min, addition of an aldehyde to the solution led to acylsilane **6**, rather than an allene silyl ether. This suggests that reverse-Brook rearrangement of **4** to **5** had taken place prior to the addition of the electrophile. Related 1,2-anionic migrations of silicon from oxygen to carbon are precedented in the preparation of allylic α-trialkylsilyl alcohols[13] and propargyl α-silyl alcohols[21] from the corresponding silyl ethers. Quenching the solution of anion **5** with water led to the volatile silaacrolein **7**.

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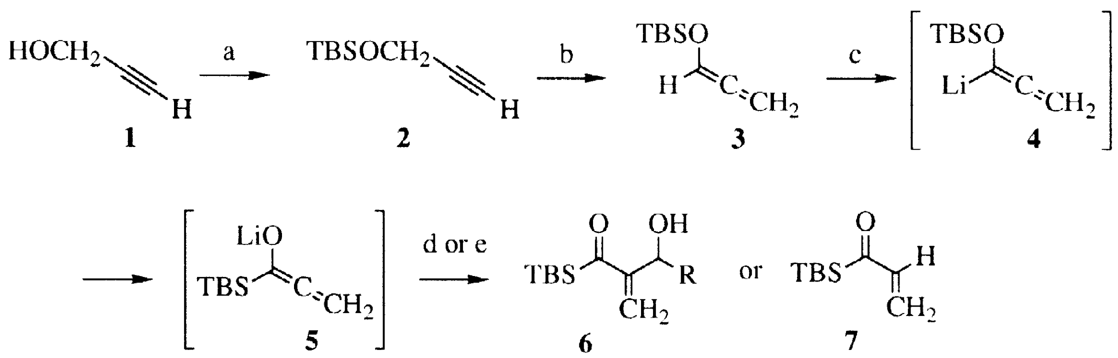
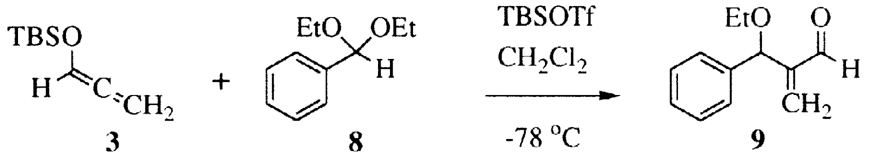
The reactivity of **5** can be assessed from the examples of Table 1. In all reactions, a small excess of the allene precursor over the aldehyde was used. Yields varied from 53% to 85%, and refer to isolated products following purification by flash column chromatography. Enolizable aldehydes gave somewhat lower yields than non-enolizable ones. Deprotonation of **3** with *n*-butyllithium gave lower yields of the acylsilanes (<30%), along with ca. 50% recovered aldehyde, however, satisfactory results in all cases were obtained through the use of *tert*-butyllithium.

Scheme 1



^{a}*t*-BuMe$_2$SiCl, imidazole, DMAP, THF, 0 °C to rt; ^{b}*t*-BuOK, 10 min at rt, 60 °C for 2 h; 68% from **1**; ^{c}*t*-BuLi, THF, -78 °C, 30 min; ^{d}RCHO, -78 °C, 30 min; ^{e}H$_2$O.

Allene **3** promises to be a versatile intermediate. For example, exposure of a mixture of **3** and benzaldehyde diethylacetal **8** in dichloromethane to catalytic *tert*-butyldimethylsilyl triflate at -78 °C quickly furnished the aldol product **9** in 53% yield (eq 1; not optimized).[22,23] In this reaction **3** functions as the synthetic equivalent of acrolein enolate.[19]

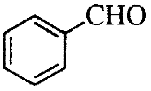
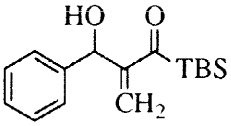
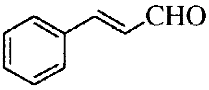
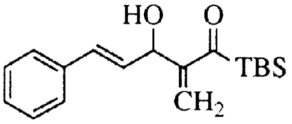
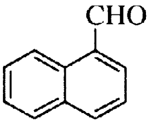
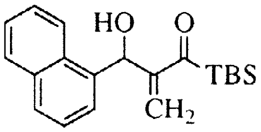
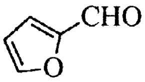
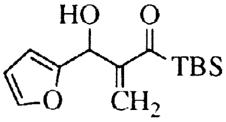
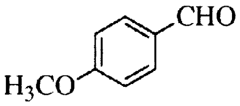
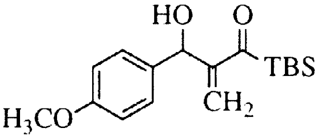
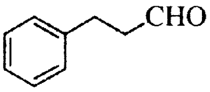
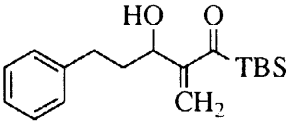
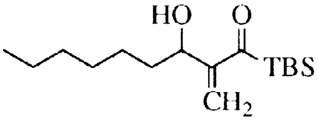
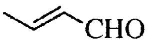
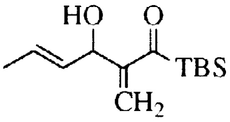
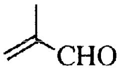
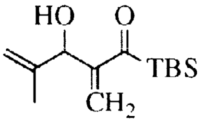


[1]

1-*Tert*-butyldimethylsilyloxy-1,2-propadiene **3**. A solution of 2.4 mL (40 mmol) of propargyl alcohol **1** in 40 mL of THF was treated with 3.4 g (50 mmol) of imidazole, 0.5 g of 4-dimethylaminopyridine (DMAP, 4 mmol) and 6.6 g (44 mmol) of *tert*-butyldimethylsilyl chloride at 0 °C. The reaction mixture was stirred at rt for 1 h, diluted with pentane, and was filtered through a short pad of silica gel. After evaporation of the solvent, 0.5 g (4 mmol) of potassium *tert*-butoxide was added at rt. The heterogeneous mixture was stirred at rt for 10 min and at 60 °C for 2 h. Distillation under reduced pressure (10 mm Hg) provided 4.6 g (68% yield from **1**) of allene **3**: IR (neat) 1960 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.60 (t, J = 5.9 Hz, 1 H), 5.25 (d, J = 5.9 Hz, 2 H), 0.93 (s, 9 H), 0.15 (s, 6 H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 204.9, 115.3, 86.6, 25.8 (3C), 18.3, -4.9 (2C).

Typical procedure for the addition of **5** to aldehydes. A solution of 220 mg of allene **3** (1.29 mmol) in 4 mL of THF was slowly treated at -78 °C with 0.70 mL of a solution of *tert*-butyllithium (1.65 M in pentane, 1.15 mmol). After 30 min, 120 µL of neat *p*-anisaldehyde (0.99 mmol) was added dropwise to the reaction

Table 1. Addition of **5** to Aldehydes

	aldehyde	acyl silane	yield
1			72%
2			78%
3			85%
4			65%
5			83%
6			58%
7			53%
8			64%
9			64%

mixture. The reaction was stirred at -78 °C for 30 min, then quenched by addition of satd aq KH_2PO_4 and diluted with ether and pentane (v/v, 1:1). Extraction with ether followed by drying (Na_2SO_4) and solvent evaporation provided the crude product which was purified by flash column chromatography on silica gel to produce the desired acylsilane (Table 1, entry 5; 255 mg, 83% yield) as a yellow oil: IR (neat) 3450, 1620, 1600, 1540 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.24 (d, J = 8.8 Hz, 1 H), 6.85 (d, J = 8.8 Hz, 1 H), 6.11 (s 2 H), 5.51 (s 1 H), 3.79 (s, 1 H), 0.86 (s, 9 H), 0.23 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 238.6, 158.8, 155.9, 133.7, 128.1, 127.7 (2C), 113.5 (2C), 71.7, 55.1, 26.5 (3C), 16.6, -4.8, -5.0; EIMS *m/z* 306 (M^+, 3%), 275 (6), 249 (49), 146 (68); exact mass calcd for $C_{17}H_{26}O_3Si$: 306.1652, found 306.1665.

To summarize, a simple and convenient method has been described for the preparation of α,β-unsaturated, α-substituted acylsilanes from allenyl silyl ether **3** which is available in two steps from propargyl alcohol. Allene **3** can serve as an equivalent of either silaacrolein or as an acrolein enolate (see eq 1). Work in progress will define the scope of both reactions, which are expected to have broad utility in synthesis.

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