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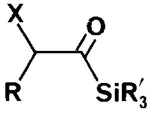
A CONVENIENT ONE-POT SYNTHESIS OF α-HALOACYLSILANES

Philip C. Bulman Page* and Stephen Rosenthal,

Department of Organic Chemistry, Robert Robinson Laboratories,
University of Liverpool, P.O.Box 147, Liverpool, L69 3BX, U.K.

Abstract: α-Bromoacylsilanes may be prepared from trimethylsilylacetylenes by hydroboration-oxidation followed by treatment of the intermediate borinate ester with *N*-bromosuccinimide.

During the course of our studies of the chemistry of acylsilanes[1,2] we discovered a need for a simple and general preparative method for α-haloacylsilanes (1).

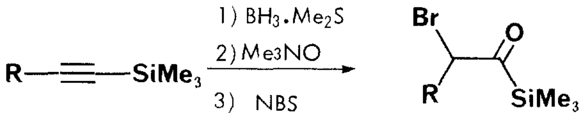


X = Br, Cl

(1)

α-Haloacylsilanes have previously been synthesised *via* a number of different routes including bromination of a 1,1-bis-trimethylsilylalkan-1-ol[3] and bromination of the silyl enol ether of an acylsilane;[4,5] however, these methods suffer from lengthy multi-step sequences, variable yields, or experimental difficulties.

We are, therefore, pleased to report a convenient synthesis of α-bromoacylsilanes from trimethylsilylacetylenes using hydroboration methodology.[6] It has been reported that enol borinates of simple aldehydes and ketones react with *N*-bromosuccinimide at 0°C to give the corresponding α-brominated species.[7] We have found that enol borinates of acyl silanes, prepared directly from silyl acetylenes *via* hydroboration-oxidation, react in a similar manner to provide α-bromoacylsilanes in moderate to good yields.



R	
$CH_3(CH_2)_4$	61%
$CH_3(CH_2)_3$	60%
$Cl(CH_2)_3$	61%
$^tBuMe_2SiO(CH_2)_3$	54%
$^tBuMe_2SiO(CH_2)_2$	52%

The entire sequence may be carried out in one pot as described below.

2-Bromohexanoyl trimethylsilane

A 2 molar solution of borane-dimethylsulphide complex in THF (7.3 mmol) was added dropwise to a solution of 1-trimethylsilylhex-1-yne (3.08g, 20 mmol) in THF (5 ml) under a nitrogen atmosphere while maintaining the temperature below 20°C. The resultant solution of trivinylborane was diluted with THF (100 ml), treated with anhydrous trimethylamine-N-oxide (2.67g, 24 mmol) at room temperature over a five minute period, and refluxed under a nitrogen atmosphere for four hours. The slurry was cooled to 0°C and purified *N*-bromosuccinimide (4.27 g, 24 mmol) added. After stirring at 0°C for between one and four hours the solvent was removed *in vacuo* and a saturated aqueous solution of ammonium chloride (100 ml) added. The aqueous layer was extracted with hexane (2 x 100 ml) and the combined organic solutions washed with water (2 x 30 ml) and dried over magnesium sulphate. Removal of the solvent and purification by column chromatography gave 2-bromohexanoyl trimethylsilane (3.0g, 60%).

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