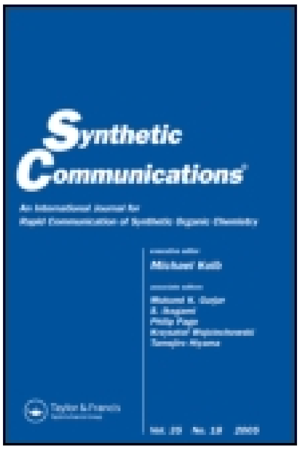

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HYDROALUMINATION AND BROMINATION OF 1-(PHENYL-SELENYL)-1-ALKYNES

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HYDROALUMINATION AND BROMINATION OF 1-(PHENYLSELENYL)-1-ALKYNES

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ABSTRACT

Hydroaluminuation and bromination of 1-(phenylselenyl)-1-alkynes were studied and compared with the rate of hydroalumination and bromination of the corresponding alkynylsilanes.

Organoselenium compounds have become an important part of organic chemistry in recent years.[1,2,3] In this paper we have studied the hydroalumination[4] and bromination[5] (Table) of 1-(phenylselenyl)-1-alkynes (**1**). Thus, the starting material, 1-(phenylselenyl)-1-alkynes (**1**), was prepared by treatment of the corresponding lithium acetylide with phenylselenyl chloride in tetrahydrofuran at −75°C for 5 min.[6]

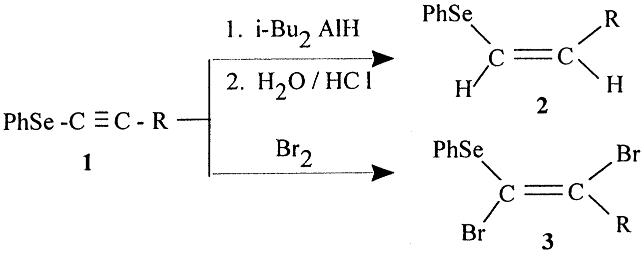
Compound **2** was prepared via hyroalumination[4] of the corresponding alkynylselenium compound (**1**). It was found that hydroalumination of alkynylselenium compound is slow (70°C, 24 h) as compared with the hydroalumination of the corresponding alkynylsilane[7,8] (40°C, 1 h). The disappearance of starting material and the appearance of product was

Table. Hydroalumination and Bromination of Alkynylselenium Compounds (**1**)

R	% Yield of Hydroalumination	% Yield of Bromination
CH_3-	75	72
$CH_3CH_2CH_2CH_2$-	77	73
C_6H_5-	78	80
P-CH_3-C_6-H_4-	73	78
THPOCH_2-	60	55
$(CH_3)_3$Si-	70	62

followed by glpc (PYE unicam series 304 chromtograph with OV1 glass column).

Compound **3** was prepared via bromination[5] of the corresponding alkynylselenium compound (**1**) at a rate similar to the bromination of the corresponding alkynylsilane[5] (−12°C/15 min).



Preparation of 1-(Phenylselenyl)-1-alkyne (1)

To a solution of 9 mmol of 1-alkyne in 9 mL of dry tetrahydrofuran (THF) was added slowly to a slight excess of LDA (1.05 equiv.) (prepared by adding an equivalent amount of *n*-butyllithium to dry diisopropylamine in dry THF at −10°C over 10 min) at −78°C. After keeping the mixture for 10 min at −78°C, 9 mL of THF solution containing 9.5 mmol of phenylselenyl chloride (equivalent to LDA or slightly in excess) was then added rapidly (reaction is instantaneous). The resulting solution was washed with an excess of 0.1 N HCl and extracted with diethyl ether. The combined organic layers were washed with saturated sodium chloride solution and dried over anhydrous sodium sulphate evaporation of solvents led to a residue which was chromatographed on 60 g of silica gel. Elution with hexane gave the desired product in high (90–95%) yield.

Hydroalumination of 1-(Phenylselenyl)-1-alkyne (1)

To a solution of 3 mmol of 1-(phenylselenyl)-1-alkyne in 3 mL of hexane was added dropwise 3.6 mL of 1 M diisobutylaluminium hydride in hexane (3.6 mmol, 1.2 eq.) at room temperature for 15 min. The reaction mixture was refluxed for 24 h. At the end of this time, the resulting mixture was poured into 0.1 N HCl and extracted with hexane. After drying over sodium sulphate, the solvent was removed by rotary evaporation to afford a residue which was chromatographed on 20 g of silica gel. Elution with hexane gave the desired product in good yield.

Bromination of 1-(Phenylselenyl)-1-alkyne (1)

To 3 mmol of 1-(phenylselenyl)-1-alkyne in 6 mL carbon tetrachloride was added dropwise 3.6 mL of 1 M solution of bromine in carbontetrachloride (1.2 equiv., 3.6 mmol) at −12°C. The reaction mixture was stirred for 0.5 h at −12°C. At the end of this time, the resulting mixture was poured into 10% sodium sulfite solution and extracted with hexane. After drying over sodium sulfate the solvent was removed by rotary evaporator to afford a residue which was chromatographed on 20 g of silica gel. Elution with hexane gave the desired product in good yield.

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