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Vicinal Difunctionalization of Alkynyl Selenides with Lithium Butylcyano Cuprate and Electrophiles

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Vicinal Difunctionalization of Alkynyl Selenides with Lithium Butylcyano Cuprate and Electrophiles

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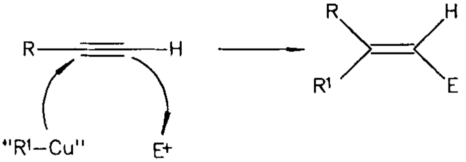
Abstract: Alkynyl selenides react with lithium butylcyano cuprate giving an intermediate lithium vinylcyano cuprate, which is trapped with electrophiles to give several classes of vinylic selenides.

Vicinal difunctionalization of acetylenes by means of organocopper or cuprates reagents is an important synthetic methodology, specially in view of the high isomeric purity of the olefinic products obtained. It is well established that the $\mathbf{R}^1$ group of the copper reagent and the electrophile are placed at the same side of the resulting double bond[1,2] (Scheme 1).

Scheme 1



In the last years, the synthesis[3] and reactivity[3b,d,e-g,i,l] of acetylenes bearing an organoseleno group (**1**) have been subject of study in our and as well as other

Table 1 - Vicinal Difunctionalization of Acetylenic Selenides

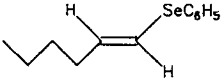
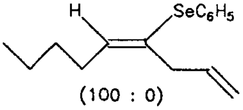
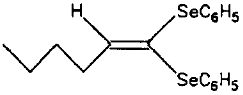
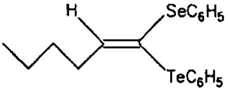
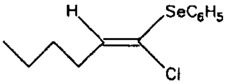
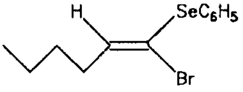
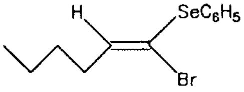
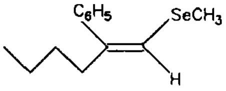
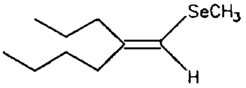
Selenoacetylene (1)	Electrophile	Product[b] (3 : 4 ratio)[c]	Yield[d] (%)
1. C_6H_5Se—≡— H[5]	NH_4Cl[e,6b]	 (87 : 13)	83
2. C_6H_5Se—≡— H	$BrCH_2CH{=}CH_2$	 (100 : 0)	75
3. C_6H_5Se—≡— H	C_6H_5SeBr[g]		76
4. C_6H_5Se—≡— H	C_6H_5TeBr[g]	 (100 : 0)	58
5. C_6H_5Se—≡— H	NCS[h]	 (100 : 0)	53

Table 1 Continued

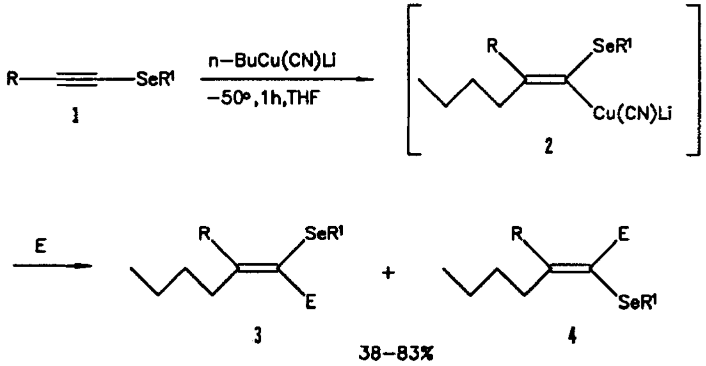
Selenoacetylene (1)	Electrophile	Product[b] (2 : 3 ratio)[c]	Yield[d] (%)
6. $C_6H_5Se-\equiv-H$	Br_2[i]	 (100 : 0)	50
7. $C_6H_5Se-\equiv-H$	NBS[h]	 (100 : 0)	63
8. $C_6H_5-\equiv-SeCH_3$[a]	NH_4Cl[6b]	 (66 : 34)	75
9.  $SeCH_3$[a]	NH_4Cl[6b]	 (100 : 0)	38

[a] Prepared as described in reference 3f; [b] The analytical data (IR, NMR, Ms) agree with the proposed structures; [c] Determined by GLC; [d] Yield of the isolated product purified by flash chromatography eluting with hexane; [e] The vinylcuprate was prepared as described in (6a) and the reaction mixture was worked up as in (6b); [f] DMF (1ml), then allylbromide (1mmol) were added to the vinyl cuprate at -30°C. The reaction mixture was stirred at room temperature for 6h; [g] HMPA (2ml), then phenylselenenylbromide or phenyltellurenylbromide (1mmol) were added to the vinyl cuprate at -60°. The reaction mixture was maintained at -60° for 2hr; [h] N-chloro- or N-bromosuccinimide (1mmol) in THF (2ml) were added to the vinyl cuprate at -78°; [i] Bromine (1mmol) in CH_2Cl_2 (2ml) was added to the vinyl cuprate at -78°C.

laboratories. In this communication, we report on the vicinal difunctionalization of **1** by the reaction with lithium butylcyano cuprate followed by capture of the intermediate vinyl cuprate **2** with several electrophiles. This process leds to di- and trisubstituted vinylic selenides **(3,4)** in reasonable to good yields with high stereoselectivity (Scheme 2).

The reaction was performed by adding n-BuLi in hexane (2.75mmol) to CuCN (2.79mmol) in THF at -50°C followed by the addition of the selenoacetylene (2mmol) in THF at the same temperature. After stirring for 1h, the electrophile was added; the stirring was continued and the reaction was worked up as indicated on Table 1.

Scheme 2



R = H,C_6H_5,C_3H_7; R¹ = Me,C_6H_5

E = NH_4Cl,CH_2=$CHCH_2Br$,C_6H_5SeBr,C_6H_5TeBr,NCS,NBS,Br_2

In this way, several classes of vinylic selenides were obtained. In all cases studied, only the regioisomer shown in Scheme 2 was obtained. This result can be rationalized in terms of a carbanion stabilization by the selenium atom[4]. Concerning the stereochemistry of the reaction, as expected for a vicinal difunctionalization of an acetylene[1,2], the isomer containing the butyl group and the electrophile at the same side of the double bond was the major one. The stereochemistry of the vinylic selenide was easily established for entry 1 (Table 1), since the ^{1}H NMR spectrum of the major isomer gives rise to a doublet at 6.41δ with a coupling constant of 14Hz typical of trans positioned protons. The proton at carbon 2 absorbs at 6.08δ as a double triplet with coupling constants of 14 and 7Hz. Typical of a trisubstituted vinylic selenide (entries 6 and 7), a

NOEDS experiment showed that irradiation of the phenyl signal increases the signal due to the vinyl proton indicating that both are on the same side of the double bond, as expected.

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5. **Preparation of Phenylselenoethyne:** Acetylene was bubbled through a solution of butylmagnesium bromide (30mmol) in THF (100ml) at -78° until the solution turned dark violet. The reaction mixture was heated to room temperature and then a solution of phenylselenenyl bromide (6.6g, 28mmol)

in THF (30ml) was added. After 30min stirring at room temperature the reaction was quenched with saturated ammonium chloride solution (20ml) and extracted with hexane (4x15ml). The organic layer was dried with magnesium sulfate, the solvents were evaporated and the residue was distilled at reduced pressure. Yield: 3.9g (78%), b.p.: 60°/0.2mmHg, ^{1}H NMR ($CDCl_3$, δ, ppm): (3,14s, 1H); 7,2-7,6 (m, 5H).

6. **Typical procedure for the vicinal difunctionalization:** a) To a suspension of CuCN (0.249g, 2.79mmol) in THF (10ml) under nitrogen at -50°C was added n-BuLi (1.1ml, 2.75mmol of a 2.5M solution in hexane). After 15min stirring the selenoacetylene (2mmol) in THF (1ml) was added. After 1h at -50°C the electrophile was added and the mixture was allowed to react as indicated in Table 1. b) Reaction with NH_4Cl: to the vinylcuprate prepared as in (**a**) was added a saturated solution of ammonium chloride (4ml). Then the mixture was diluted with hexane (10ml) and the aqueous phase was extracted twice with hexane (2x10ml). The combined extracts were washed with ammonium hydroxide solution, water and brine, the organic phase was dried over magnesium sulfate, the solvent was evaporated and the residue was flash cromatographed on silica eluting with hexane.

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