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## Cu(I)-CATALYZED REACTION OF TERMINAL ALKYNES WITH PHENYL SELENOCYANATE IN THE PRESENCE OF TRIETHYLAMINE. SYNTHESIS OF ALKYNYL SELENIDES<sup>1</sup>

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Summary: Treatment of terminal alkynes with phenyl selenocyanate in dichloromethane in the presence of CuX(X=CN or Br) and triethylamine at room temperature gave l-phenylseleno-l-alkynes in high yields.

Certain transition metal ions, especially  $Hg(II)^2$ ,  $Cu(I)^3$ , and  $Cu(II)^{3,4}$ , have been known to effectively promote reactions involving organoselenium reagents<sup>5</sup> which are relatively unreactive under ordinary conditions. For instance, unlike benzeneselenenyl halides, phenyl selenocyanate  $(1)^6$  is totally inert by itself toward carbon-carbon multiple bonds<sup>7</sup>, although it reacts not only with unactivated olefins<sup>3b</sup> but with alkynes irreversibly by the assistance of appropriate copper salts. Thus, we reported in the previous communication that copper(II) salts(CuBr<sub>2</sub> or CuCl<sub>2</sub>)-assisted reaction of phenyl selenocyanate (<u>1</u>) with alkynes in the presence of a catalytic amount of triethylamine provided halogen-substituted vinyl selenides (<u>2</u>) in decent yields.<sup>4</sup>(Eq.1)

$$R-C=C-R' \xrightarrow{PhSeCN (1)} R(X)C=C(R')SePh (1)$$

$$CuX_2-Et_3N/CH_2Cl_2 (X = Cl or Br) \xrightarrow{2}$$

We now report entirely different reactivity of  $\underline{1}$  with terminal alkynes ( $\underline{3}$ ) in the presence of copper(I) salt and triethylamine.(Eq.2) The reaction provides a very simple and efficient procedure for general synthesis of 1-phenylseleno-1-alkynes ( $\underline{4}$ ).

H-C=C-R 
$$\xrightarrow{\text{PhSeCN}(\underline{1})}$$
 PhSe-C=C-R + HCN (2)  
CuX-Et<sub>3</sub>N/CH<sub>2</sub>Cl<sub>2</sub>  
3 (X = CN or Br) 4

In a typical experiment,<sup>8</sup> triethylamine(0.9 ml, 6.5 mmol) was added to a ternary mixture of alkyne ( $\underline{3}$ , 3.3 mmol), phenyl selenocyanate ( $\underline{1}$ , 608 mg, 3.3 mmol)<sup>6</sup> and copper(I) salt (CuCN 892 mg, 10 mmol or CuBr 238 mg, 1.7 mmol)<sup>9</sup> in dichloromethane (10 ml) at room temperature under argon and the mixture was vigorously stirred at this temperature until all phenyl selenocyanate ( $\underline{1}$ ) had been consumed (TLC control, hexane as eluent). The mixture was then filtered through a silica-gel column(2x10 cm) using hexane-ether mixture as an eluent. The filtrate(200 ml) was concentrated <u>in vacuo</u> to provide spectrally pure 1-phenylseleno-1-alkyne ( $\underline{4}$ ) as a colorless oil in the yield shown in the Table. Further purification to obtain samples of analytical purity was achieved by chromatography on a medium pressure column using silica gel(5 g of German Merck Kieselgel 60, 230-400 mesh).

As shown in the Table, yields were uniformly excellent(86-96%) except for the case of ethyl propiolate(37%, 4g)<sup>10</sup> using either copper(I) salt. It was shown that the reaction is catalytic in Cu(I); the amount of CuCN could be reduced to 10 mol%(72% yield, 72 h at  $25^{\circ}$ C). In practice, however, a large excess CuCN, an inexpensive reagent, was employed in order for the reaction to complete in a short period at room temperature. It is seen from the Table that (a) the catalytic activity of CuBr is much higher than that of CuCN and (b) alkynols (4e and 4f) are considerably less reactive than the unfunctionalized alkynes (4a-4d) under these conditions, although yields are comparable.

Structures of these selenoalkynes (<u>4</u>) were assigned on the basis of spectroscopic data(IR, <sup>1</sup>H- and <sup>13</sup>C-NMR) and elemental analyses(C and H). For example, as listed in the Table, <sup>13</sup>C-NMR chemical shifts of sp-carbons were 57.32-74.96(singlet,  $\equiv$ <u>C</u>-C) and 96.38-107.31(singlet, Se-<u>C</u> $\equiv$ ) and IR spectra showed weak to medium bands between 2150 and 2180 cm<sup>-1</sup> due to the triple bonds.

Mechanistically, the present reaction may be rationalized by the intermediacy of copper acetylide ( $\underline{5}$ ) as shown in the following scheme. It is known that the reaction of terminal alkynes with copper(I) salts in the presence of an amine provides copper(I) acetylide ( $\underline{5}$ ).<sup>11</sup> "Soft-soft" metal interaction between copper and selenium could then facilitate the reaction of  $\underline{5}$  with phenyl selenocyanate ( $\underline{1}$ ) to afford 1-selenoalkyne ( $\underline{4}$ ) and CuCN. The latter would be used again to regenerate copper(I) acetylide  $\underline{5}$ . The first step( $\underline{3} \rightarrow \underline{5}$ ) would most probably be the rate determining step since the efficacy of the copper(I) species(CuCN and CuBr) follows the order generally observed for the related reactions involving copper(I) acetylide.<sup>11b</sup>

H-C=C-R + CuX 
$$\xrightarrow{\text{Et}_{3}N}$$
 Cu-C=C-R + HX  
 $3 \xrightarrow{1}$   $(X = CN \text{ or } Br)$  Cu-C=C-R + HX  
HX  $(-HCN)$   $\xrightarrow{1}$  PhSeCN  $1$   
CuCN + PhSe-C=C-R  
 $4$ 

Compound	R	CuX (mol/mol of <u>1</u> )	Reaction time	Yield <mark>b</mark> (%)	IR <sup>C</sup> ν(cm <sup>-1</sup> )	<sup>13</sup> C-NMR <sup>d</sup> δ
<u>4</u> a	(CH <sub>2</sub> ) <sub>3</sub> Me	CuCN(3.0)	2 h	93	2170	104 51 57 43
		CuBr(0.5)	10 min	95	2170	104.31, 37.43
<u>4</u> b	(CH <sub>2</sub> ) <sub>2</sub> CHMe <sub>2</sub>	CuCN(3.1)	2 h	91	0100	
		CuBr(0.5)	10 min	96	2180	104.56, 57.32
<u>4</u> c	(CH <sub>2</sub> ) <sub>5</sub> Me	CuCN(2.8)	2.5 h	94		
		CuBr(0.7)	10 min	88	2180	104.56, 57.43
<u>4</u> d	(CH <sub>2</sub> )7 <sup>Me</sup>	CuCN(3.0)	2.5 h	90		
		CuBr(1.0)	5 min	94	2180	104.75, 57.49
<u>4</u> e	C(OH)(Me)CH <sub>2</sub> Me	CuBr(0.4)	2 h	86	2165	107.31, 62.84
<u>4</u> f	сн <sub>2</sub> он	CuBr(0.5)	2 h	92	2180	101.96, 65.99
<u>4</u> g	COOEt	CuBr(1.0)	1 h	37	2150	96.38, 74.76

TABLE Synthesis and Spectral Data of 1-Phenylseleno-1-alkynes  $(4)^{\frac{a}{2}}$ 

 $\frac{a}{S}$ See text for detailed experimental conditions. All reactions were run in carefully dried dichloromethane(distilled from calcium hydride under argon and stored over molecular sieves).  $\frac{b}{I}$ Solated yield of spectrally pure products.  $\frac{c}{M}$ Measured as a neat liquid. The listed data indicate weak to medium absorption bands due to carbon-carbon triple bond stretching vibration.  $\frac{d}{M}$ Measured in CDCl<sub>3</sub> at 22.5 MHz with tetramethylsilane as an internal standard. The listed data indicate chemical shifts of sp-carbons which show up as singlets in off-resonance spectra.

Although alkynyl selenides ( $\underline{4}$ ) have been prepared by generating acetylide anion with <u>n</u>-butyllithium followed by treatment with benzeneselenenyl halide,<sup>12</sup> we believe that the present reaction is more useful than the conventional procedure because of its mildness, experimental simplicity and functional group compatibility(hydroxyl and ethoxycarbonyl in this case).

Finally it may be worth mentioning that  $\underline{4}$  can be regarded as a synthetic equivalent of a ketene and that their selenoxides may serve as excellent Michael acceptors and dienophiles in the Diels-Alder reaction.<sup>13</sup> Research along these lines are now underway.

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