CHEMISTRY LETTERS, pp. 253-256, 1982.

Cu(I)-CATALYZED REACTION OF TERMINAL ALKYNES WITH PHENYL SELENOCYANATE IN THE PRESENCE OF TRIETHYLAMINE. SYNTHESIS OF ALKYNYL SELENIDES[1]

Shuji TOMODA*, Yoshito TAKEUCHI, and Yujiro NOMURA

Department of Chemistry, College of General Education
The University of Tokyo, Komaba, Meguro-Ku, Tokyo 153

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 1-phenylseleno-1-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[5] 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 [7], although it reacts not only with unactivated olefins[3b] but with alkynes irreversibly by the assistance of appropriate copper salts. Thus, we reported in the previous communication that copper(II) salts($CuBr_2$ or $CuCl_2$)-assisted reaction of phenyl selenocyanate (1) with alkynes in the presence of a catalytic amount of triethylamine provided halogen-substituted vinyl selenides (2) in decent yields.[4](Eq.1)

$$\text{R-C}\equiv\text{C-R'} \xrightarrow[\substack{\text{CuX}_2\text{-Et}_3\text{N/CH}_2\text{Cl}_2 \\ (\text{X = Cl or Br})}]{\text{PhSeCN }(\underline{1})} \underset{\underline{2}}{\text{R(X)C=C(R')SePh}} \qquad (1)$$

We now report entirely different reactivity of 1 with terminal alkynes (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 (4).

$$\underset{\underline{3}}{\text{H-C}\equiv\text{C-R}} \xrightarrow[\substack{\text{CuX-Et}_3\text{N/CH}_2\text{Cl}_2 \\ (\text{X = CN or Br})}]{\text{PhSeCN }(\underline{1})} \underset{\underline{4}}{\text{PhSe-C}\equiv\text{C-R}} + \text{HCN} \qquad (2)$$

In a typical experiment,[8] triethylamine(0.9 ml, 6.5 mmol) was added to a ternary mixture of alkyne (3, 3.3 mmol), phenyl selenocyanate (1, 608 mg, 3.3 mmol)[6] and copper(I) salt (CuCN 892 mg, 10 mmol or CuBr 238 mg, 1.7 mmol)[9] in dichloromethane (10 ml) at room temperature under argon and the mixture was vigorously stirred at this temperature until all phenyl selenocyanate (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 *in vacuo* to provide spectrally pure 1-phenylseleno-1-alkyne (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)[10] 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°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 (4) were assigned on the basis of spectroscopic data(IR, ^{1}H- and ^{13}C-NMR) and elemental analyses(C and H). For example, as listed in the Table, ^{13}C-NMR chemical shifts of sp-carbons were 57.32-74.96(singlet, ≡C-C) and 96.38-107.31(singlet, Se-C≡) and IR spectra showed weak to medium bands between 2150 and 2180 cm^{-1} due to the triple bonds.

Mechanistically, the present reaction may be rationalized by the intermediacy of copper acetylide (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 (5).[11] "Soft-soft" metal interaction between copper and selenium could then facilitate the reaction of 5 with phenyl selenocyanate (1) to afford 1-selenoalkyne (4) and CuCN. The latter would be used again to regenerate copper(I) acetylide 5. The first step(3 → 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.[11b]

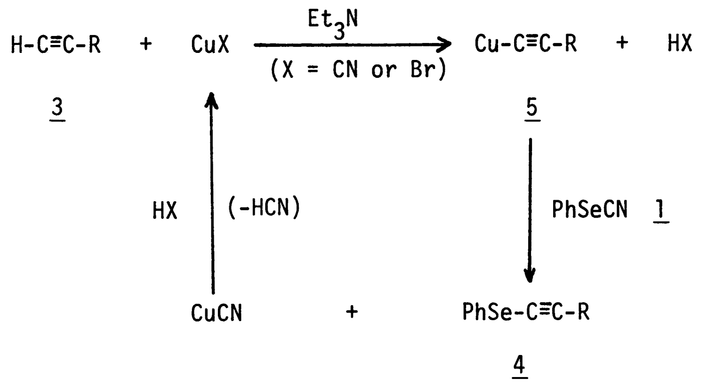

TABLE Synthesis and Spectral Data of 1-Phenylseleno-1-alkynes (4)[a]

Compound	R	CuX (mol/mol of 1)	Reaction time	Yield[b] (%)	IR[c] ν(cm^{-1})	^{13}C-NMR[d] δ
4a	$(CH_2)_3Me$	CuCN(3.0)	2 h	93	2170	104.51, 57.43
		CuBr(0.5)	10 min	95		
4b	$(CH_2)_2CHMe_2$	CuCN(3.1)	2 h	91	2180	104.56, 57.32
		CuBr(0.5)	10 min	96		
4c	$(CH_2)_5Me$	CuCN(2.8)	2.5 h	94	2180	104.56, 57.43
		CuBr(0.7)	10 min	88		
4d	$(CH_2)_7Me$	CuCN(3.0)	2.5 h	90	2180	104.75, 57.49
		CuBr(1.0)	5 min	94		
4e	$C(OH)(Me)CH_2Me$	CuBr(0.4)	2 h	86	2165	107.31, 62.84
4f	CH_2OH	CuBr(0.5)	2 h	92	2180	101.96, 65.99
4g	COOEt	CuBr(1.0)	1 h	37	2150	96.38, 74.76

[a] 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). [b] Isolated yield of spectrally pure products. [c] Measured as a neat liquid. The listed data indicate weak to medium absorption bands due to carbon-carbon triple bond stretching vibration. [d] Measured in $CDCl_3$ 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 (4) have been prepared by generating acetylide anion with *n*-butyllithium followed by treatment with benzeneselenenyl halide,[12] 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 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.[13] Research along these lines are now underway.

ACKNOWLEDGEMENT: We thank the Ministry of Education for the purchase of JEOL FX-90Q NMR spectrometer used in this work.

REFERENCES

1. Organoselenium Chemistry Part 4. Part 3; reference 4.
2. A. Kozikowski and A. Ames, J. Org. Chem., 43, 2735(1978).
3. (a) A. Kozikowski and A. Ames, J. Am. Chem. Soc., 102, 860(1980); (b) A. Toshimitsu, T. Aoai, S. Uemura, and M. Okano, J. Org. Chem., 46, 3021(1981) and references cited therein.
4. S. Tomoda, Y. Takeuchi, and Y. Nomura, Chem. Lett., 1981, 1715.
5. For recent reviews on organoselenium chemistry, see; (a) H.J. Reich, Acc. Chem. Res., 12, 22 (1979); (b) D.L.J. Clive, Tetrahedron, 34, 1049(1978); (c) H.J. Reich,"Oxidation in Organic Chemistry. Part C", W. Trahanovsky, Ed., Academic Press, New York, 1978, p.1.
6. For a new efficient synthesis of this compound, see; S. Tomoda, Y. Takeuchi, and Y. Nomura, Chem. Lett., 1981, 1069.
7. Phenyl selenocyanate (1) is a chromatographically stable compound. Its reaction with oxygen compounds in the absence of transition metal salts have been fully exploited; (a) P.A. Grieco, S. Gilman, and M. Nishizawa, J. Org. Chem., 41, 1485(1976); (b) M. Sevrin and A. Krief, J. Chem. Soc. Chem. Commun., 1980, 656; (c) P.A. Grieco and Y. Yokoyama, J. Am. Chem. Soc., 99, 5210(1977); (d) P.A. Grieco, Y. Yokoyama, and E. Williams, J. Org. Chem., 43, 1283(1978); (e) P.A. Grieco, J.Y. Jaw, D.A. Claremon, and K.C. Nicolaou, J. Org. Chem., 46, 1215(1981).
8. The reaction must be carried out in a well-ventilated hood to avoid hazard from concomitant evolution of extremely toxic hydrogen cyanide gas.
9. Commercial reagents were used without further purification.
10. Examination of TLC before and after workup indicated the presence of pure 4g, which was indefinitely stable at room temperature. Reduction of the yield may therefore be due to some kind of complex formation of 4g or of secondary product(s) with copper(I) salt either before or during workup.
11. (a) T.P. Lockhart, P.B. Comita, and R.G. Bergman, J. Am. Chem. Soc., 103, 4082(1981); (b) C.E. Castro, E.J. Gaughan, and D.C. Owsley, J. Org. Chem., 31, 4071(1966).
12. (a) N. Petragrani, R. Rodrigues, and J.V. Comasseto, J. Organometal. Chem., 114, 281(1976); (b) S. Raucher, M.R. Hansen, and M.A. Colter, J. Org. Chem., 43, 4885(1978).
13. The Diels-Alder reaction of the sulfur analogue of the selenoxide of 4g has been reported very recently: M. Shen and A.G. Schultz, Tetrahedron Lett., 22, 3347(1981). Utility of 4 may be enhanced by recent reports on the efficient synthesis of terminal alkynes having a variety of functional groups; (a) E. Negishi, A.O. King, W.L. Klima, W. Patterson, and A.Silveira, Jr., J. Org. Chem., 45, 2526(1980); (b) E.V. Dehmlow and M. Lissel, Tetrahedron, 37, 1653(1981).

(Received December 28, 1981)