CHEMISTRY LETTERS, pp. 1715-1718, 1981.

AMINE-CATALYZED 1,2-HALOSELENENYLATION OF ALKYNES WITH PHENYL SELENOCYANATE IN THE PRESENCE OF CUPRIC HALIDE[1]

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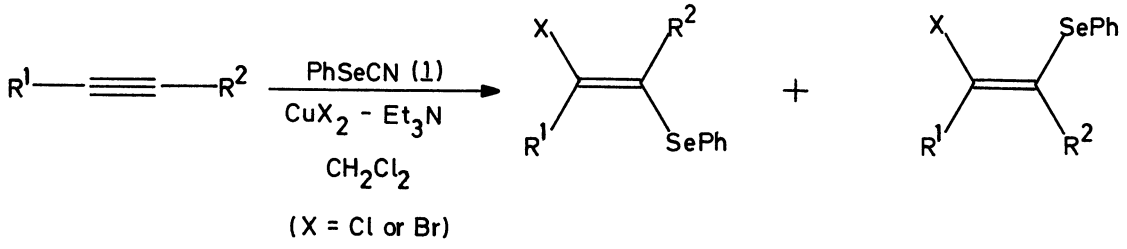
The reaction of phenyl selenocyanate with six common alkynes in the presence of cupric halide(halogen=Cl or Br) and triethylamine provided halogen-substituted vinyl selenides, 1,2-haloselenenylation products, in 66-96% yields.

Activation of organometalloids by transition metal salts is commonly recognized as a highly effective means to overcome otherwise unrealistic reaction pathways.[2] The technique has recently been introduced successfully in organoselenium chemistry, one of the most fruitful areas of modern organic synthesis.[3] For instance, it is known that by analogy to organosulfur compounds[2a], organoselenium reagents are often activated by Hg(II)[4], Cu(I) or Cu(II)[4,5] as a result of "soft-soft" metal interaction.[6] Thus, even relatively inert selenium species like phenyl selenocyanate (1) can be made highly reactive by the assistance of copper salts.[5b] In an extension of our convenient synthesis of 1[7], we wish to describe herein the title reaction as a novel application of 1 to the syntheses of halogen-substituted vinyl selenides (3).



2 3(E) 3(Z)

In an initial attempt, alkynes (2) were treated with 1 in a series of organic solvents at ambient temperatures in the presence of a large excess cupric halide (halogen=Cl or Br), but no reaction had occurred after 24 h stirring(TLC control). However, upon addition of a catalytic amount of triethylamine to the reaction mixture, a slow but clean reaction started. Of the organic solvents examined, dichloromethane gave the most satisfactory results both in terms of the yield and the rate of the reaction.[8] In a typical procedure, triethylamine(140 µl, 101 mg, 1.0 mmol) was dropwise added at 26°C under argon to a ternary mixture of an alkyne (2.0 mmol), phenyl selenocyanate(1, 425 mg, 2.2 mmol) and cupric halide(4.0 mmol) in dichloromethane(8 ml). After having been stirred for 24 h, the reaction mixture was filtered through a silica-gel column(5 g, 1x15 cm column) eluting with hexane. The eluent(50 ml) was concentrated and the residue chromatographed on a medium-pressure column(5g of German Merck Kieselgel 60, 230-400 mesh) eluting with hexane to provide the corresponding vinyl selenide (3) as a colorless oil in 66-96% yield.

Pertinent data are collected in the Table. It is first noted that the reactions involving internal alkynes(entry 1, 2 and 3) were particularly clean(TLC control) and provided nearly quantitative yields of the vinyl selenides (3), whereas those involving terminal slkynes(entry 4,5,6, and 7) were somewhat less clean. As indicated in the Table, in each case except for entry 2 and 3, the product 3 was found to be a chromotographically inseparable mixture of two isomers (of the four possible isomers) as revealed by ^{13}C-NMR analysis. The structures of these products were consistent with their IR($\nu_{C=C}$ 1597-1612 cm^{-1}), where appcicable, with ^{1}H-NMR(vinyl proton, δ=6.28-6.51), ^{13}C-NMR(=CHCl carbon, doublet, δ=114.59-118.70) and elemental analyses(C,H, and Cl or Br). Furthermore independent synthesis of compound 3(except 3c) from alkynes 2 and benzeneselenenyl chloride[9] unequivocally established the primary structure assigned to 3. In the case of unsymmetrical internal alkyne(entry 1), we are only assuming that the two products are regioisomers rather than geometrical(configurational)isomers. Support for this hypothesis is provided by the observation that the product derived from symmetrical alkyne(entry 2 and 3, 4-octyne) is a single isomer, which is most likely to be an E isomer on steric grounds. Therefore the reactions of internal alkynes may be stereospecific but not regiospecific.

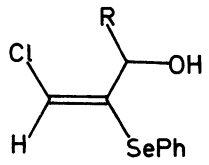
The two isomers arising from each terminal alkyne(entry 4,5,6, and 7) must be geometrical isomers because of the relatively low chemical shifts of the vinylic

Table Synthesis of chloro(or bromo)-phenylselenoalkenes (3)[a]

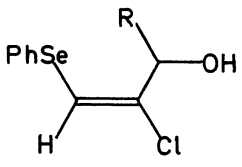
entry	compound no.	R^1	R^2	X	yield(%)[b]	isomer ratio[c] E : Z
1	3a	CH_3CH_2	or $(CH_2)_5CH_3$	Cl	93	[d]
2	3b	$CH_3CH_2CH_2$	$CH_3CH_2CH_2$	Cl	96	100 : 0[e]
3	3c	$CH_3CH_2CH_2$	$CH_3CH_2CH_2$	Br	92	100 : 0[e]
4	3d	H	$(CH_2)_3CH_3$	Cl	66	86 : 14
5	3e	H	$(CH_2)_2CH(CH_3)_2$	Cl	80	72 : 28
6	3f	H	$(CH_2)_5CH_3$	Cl	83	75 : 25
7	3g	H	$(CH_2)_7CH_3$	Cl	76	82 : 18

[a]See text for reaction conditions. Structure assignments of these compounds were based on proton and carbon NMR, IR and elemental analyses. [b]Isolated yield. [c]Determined by proton NMR integration of vinylic protons. Major isomers were assigned to E according to reference 11. [d]Obtained as a mixture of two regioisomers (56:44)(See text for details). [e]See text.

protons(δ=6.28-6.51) and the small chemical shift difference between the terminal sp^2-carbons of the isomers(Δδ=3.66-3.80); the possibility of regioisomer may be eliminated by the following two reasons[10]: (a) the chemical shift of the vinyl proton in (E)-1-chloro-2-phenylseleno-1-alkenes (4a, R=alkyl) falls in the range of δ=6.20-6.47, and the chemical shift of the vinyl proton in (E)-2-chloro-1-phenylseleno-1-alken-3-ols (4b, R=alkyl) falls in the range of δ=5.70-5.92, and (b) the average ^{13}C chemical shift difference between the terminal sp^2-carbons in the regioisomers 4a and 4b is Δδ=10.3. Although we are again assuming that the allylic OH in 4 should not greatly affect the chemical shift of terminal vinyl protons and carbons, such stereochemical assignments of product 3 are in agreement with the previous report by others on the reaction of benzeneselenenyl chloride with hydroxyalkynes.[11]



4a



4b

Several reports have recently appeared on the synthesis of halogen-substituted phenylselenoalkenes,[9-11] but benzeneselenenyl halides have been employed as the selenium source without exception. Although the procedure described here is comparable to these previous methods both with respect to the yield and isomer ratio, the implication of our reaction is significant in that the halogen atom comes from the cupric halides. In this connection, the present procedure can in principle be extended to the synthesis of a variety of substituted vinyl selenides by deliberate choice of other cupric salts. Efforts are currently being made toward this goal.

ACKNOWLEDGEMENT: We thank the Ministry of Education for support of this research through Research Grant for Promotion of Science.

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(Received October 6, 1981)