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Stereo and Regioselective Synthesis of *(Z)*-β–Arylseleno-α,β-Unsaturated Ketones *via* Selenocarbonylation Addition of Arylselenoesters to Alkynes Catalyzed by Copper(I)

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Abstract: Selenocarbonylation addition reaction of selenoesters to nonactived terminal alkynes under the catalysis of CuX produces *(Z)*-β–arylseleno-α,β–unsaturated ketones in high selectivity and high yields. The mechanism of this reaction is also discussed.

Vinyl selenides, because of the varied reactivity of their selenium atoms, became important precursors of many kinds of organic compounds, particularly substituted alkenes that occur in many biologically active compounds as a skeleton structure.[1,2] There have been several reviews about the preparation and application of vinyl selenides.[3-5] The synthesis of vinyl selenides linked to electron-withdrawing-groups, such as carbonyl, cyano, etc., have scarcely been reported.[6-8] Now we have developed a practical method for preparation of vinyl selenides linked to carbonyl *via* selenocarbonylation addition of selenoesters to alkynes catalyzed by copper(I) halide, introducing seleno and carbonyl groups into organic molecules simultaneously.

Reaction of alkynylcoppers and selenoesters

We first studied the reaction of the copper(I) salt of alkynes with selenoesters **1**. As nucleophilic reagents, alkynylcoppers **2** attacked selenoesters at the carbonyl carbon atom, forming α,β–alkynones **3**. The Cu(I) ions combined with the anions of selenides to form copper arylselenides **4**, which were converted to arylselenols after acidification and added to α,β–alkynones nucleophilically to produce *(Z)*–β-arylseleno–α,β-unsaturated ketones **5** (Scheme 1). The results of this reaction are presented in Table 1 as Method A.

The products **5** were proved to be (*Z*)-configuration from the oxidation of **5a** with iodine under basic condition. In this oxidation reaction, product **5a** was converted to (*2Z*)-β-phenylselenocinnamic acid, which

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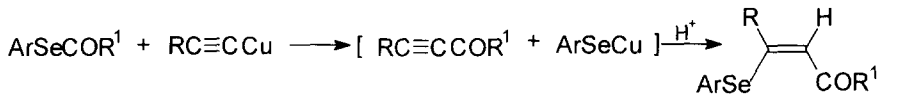


1 2 3 4 5

Scheme 1

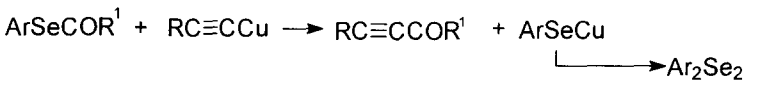
has the same melting point and IR, ^{1}H-NMR spectra data with those reported.[9] We did not isolate *(E)*-configuration products in the above procedure.

Table 1. Synthesis of *(Z)*-β–arylseleno-α,β-unsaturated ketones.

Products	R	R^1	Ar	Yields(%)[a]	
				Method A[b]	Method B[c]
5a	Ph	Ph	CH_3	94	88
5b	Ph	*p*-ClC_6H_4	Ph	93	83
5c	CH_3OCH_2	*p*-ClC_6H_4	Ph	89	92
5d	CH_3OCH_2	*p*-$CH_3OC_6H_4$	Ph	82	81
5e	Ph	*p*-$CH_3OC_6H_4$	Ph	85	84
5f	$PhCO_2CH_2$	*p*-ClC_6H_4	Ph	77	--

a: Isolated yields. b: Reaction of alkynylcoppers and selenoesters. c: Addition of selenoesters to alkynes.

For proving the mechanism of the above reaction, we tried to isolate **3** and **4** by interrupting the reaction at the stage of disappearance of selenoesters. The reactive mixture was filtered, the filtrates gave α,β-alkynones **3** after purification, and the solids were oxidized to diarylselenides **6** after exposing to air and washing with the ammonia solution. Compounds **3** and **6** were characterized by IR, NMR and other spectra data.(Scheme 2)



1 2 3 6

Scheme 2

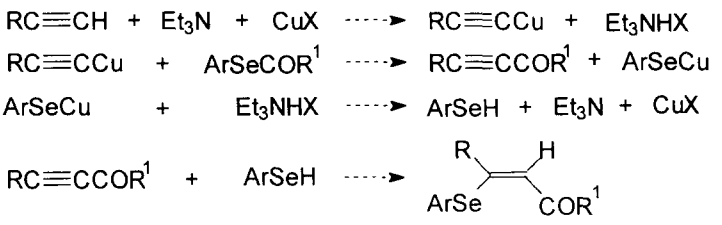
Table 2. Reaction of alkynylcoppers and selenoesters.

Ar	R^1	R	Yields of **3** (%)[a]	Yields of **6** (%)[a]
Ph	CH_3	Ph	88	92
p-ClC_6H_4	Ph	Ph	93	96

a: Isolated yields.

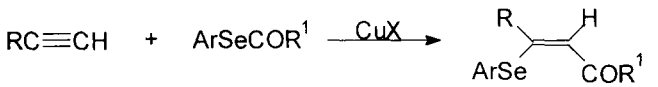
Addition of selenoesters to alkynes

Considering the results of the above reaction, we assumed that CuX and alkynes would form alkynylcoppers in the presence of organic base, which would react with selenoesters in a similar fashion to that shown in Scheme 1. The HX, produced in this procedure, would convert the intermediates **4** to arylselenols, which would then add to α,β-alkynones **3** to form the addition products **5**. (Scheme 3)



Scheme 3

The experimental results indicated that when the reaction of selenoesters and alkynes **7** proceeded in the presence of triethylamine and CuX, we only isolated α,β-alkynones **3**, rather than the addition products **5.** We estimated that the acidification and addition of **4** to α,β-alkynones **3** would be the rate-controlling steps of the reaction. Thus we used trimethylamine hydrochloride instead of triethylamine to ensure that **4** is converted to arylselenol and adds to **3** as quickly as possible, under these conditions the reaction of selenoesters and alkynes proceeded smoothly, producing the addition products **5** with high stereo and regioselectivity and in high yields[10] (Scheme 4). The results are also presented in Table 1 as Method B.



7 **2** **5**

Scheme 4

Just like the addition reaction of selenophenols to the alkynes linked to electron withdrawing groups, this reaction proceeded *via* nucleophilic addition and also produced (*Z*)-products only.[9]

This reaction is a kind of bifunctional addition reaction, the two functional groups, seleno and carbonyl, were introduced into organic molecules simultaneously. This procedure provided a practical method for stereo and regioselectively synthesis of *(Z)*-β-arylseleno–α,β-unsaturated ketones.

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10.Typical procedure for addition of selenoesters to alkynes: **Method A:** The alkynylcoppers(10mmol) and selenoesters(10mmol) were heated at 80-100°C in 10ml anhydrous DMF for 8-24h under N_2. Trimethylamine hydrochloride (10mmol) was added after cooling to room temperature. The mixture was heated at 50-60°C for 4h. Then ether (20ml) was added after cooling and the mixture was filtered. The filtrates were extracted with ether three times. The organic phase was washed with water, and dried over Na_2SO_4. The solvent was removed *in vacuo* and the residues were recrystallized from ether. **Method B:** Under N_2, the mixture of selenoesters (10mmol), alkynes (10mmol, for 3-methoxyl-1-propynene, using 15mmol), trimethylamine hydrochloride (10mmol), and CuX(X=Cl or I, 2.5mmol) in 20ml DMF were heated at 80-90 ℃ for 6-8h. Then the solution of NH_4Cl (30ml) was added after cooling. The purification of products was the same as Method A. **5a**, mp104-107°C; ^{1}H-NMR(ppm), 2.16(s,3H), 6.62(s, 1H), 6.73-7.20(m, 10H); IR(cm^{-1}), 1670, 1550, 1496, 1450, 1230, 1185, 990, 830, 760; MS(m\e), 302(M^+, 44.76). **5b**, mp168-171°C; ^{1}H-NMR(ppm), 6.74-7.23(m, 8H), 7.25-7.56(m, 5H), 7.84-8.33(m, 2H); IR(cm^{-1}), 1635, 1610, 1588, 1534, 1496, 1396, 1240, 1090, 1048, 1030, 1015, 946, 810, 780; MS(m\e), 398(M^+, 14.37). **5c**, mp111-112°C, ^{1}H-NMR(ppm), 3.13(s, 3H), 3.70(s, 2H), 7.30-7.75(m, 8H), 7.80-8.10(m, 2H); IR(cm^{-1}),1640, 1604, 1585, 1540, 1342, 1300, 1240, 1125, 1088, 1014, 862, 820, 776; MS(m\e), 366(M^+, 26.37). **5d**, mp76-78°C; ^{1}H-NMR(ppm), 3.13(s, 3H), 3.67-3.83(d, 5H), 6.63-6.90(m, 2H), 7.20-7.67(m, 6H), 7.83-8.06(m, 2H). **5e**, mp162-164°C; ^{1}H-NMR(ppm), 3.60(s, 3H), 6.50-7.73(m, 13H), 7.76-8.36(m, 2H); IR(cm^{-1}), 1652, 1610, 1590, 1480, 1460, 1322, 1290, 1215, 1175, 1090, 1010, 812, 768; MS (m\e), 394(M^+, 23.96). The above products also gave satisfactory elemental analysis.