Pergamon

Tetrahedron 55 (1999) 13201–13204

TETRAHEDRON

Copper-Catalyzed Carbonylative Cross-Coupling of (E)-α-Selanylvinylzirconiums with Alkynyliodonium Tosylates

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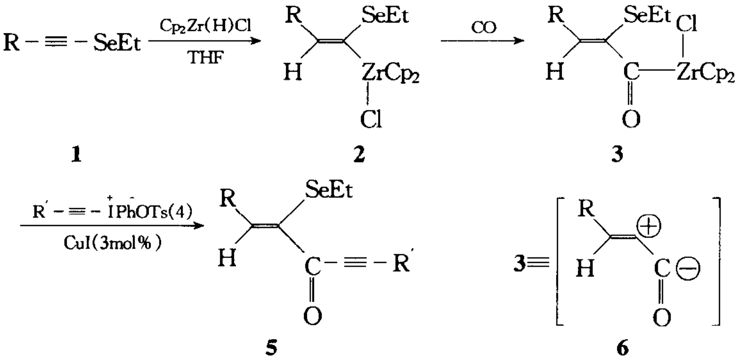
Received 8 June 1999; revised 27 August 1999; accepted 9 September 1999

***Abstract*:** The copper-catalyzed carbonylative coupling of (E)-α-selanylvinylzirconiums with alkynyliodonium tosylates at r.t. in THF in the presence of 3 mol% CuI, and atmospheric pressure of carbon monoxide for 15 min. afforded in fair to good yields the cross-coupled ketone products. © 1999 Elsevier Science Ltd. All rights reserved.

Easy access to stable acylzirconocene chloride derivatives through a sequential treatment of alkenes or alkynes with zirconocene hydrochloride ([Cp_2ZrHCl], Schwartz reagent) and carbon monoxide has brought about the synthetic utility of acylzirconiums for the preparation of carboxylic acids and their derivatives.[1] Sometimes the utility of this route is limited by the requirement of a high pressure of carbon monoxide and long reaction time.[1] To seek alternatives to this method, we have investigated copper-catalyzed carbonylative cross-coupling of alkynyliodonium tosylates with (E)-α-selanylvinylzirconiums. The recent synthetic applications of hypervalent iodine compounds are due to their ready availability and nontoxic properties.[2,3,4] Transmetalation of organic ligands from zirconium to copper has become a very intensely researched process due to the wide application of organocopper reagents in synthetic chemistry.[5,6] Vinylselenides are important synthetic intermediates.[7] Disubstituted alkenyl selenides are synthetically equivalent to carbonyls and can be stereospecifically converted to trisubstituted alkenes by nickel – catalyzed couplings reactions with Grignard reagents.[8] As an extension of our studies, herein we wish to report the copper-catalyzed couplings of alkynyliodonium salts with (E)-α-selanylvinylzirconiums in the presence of an atmospheric pressure of carbon monoxide under mild conditions, which were complete in 15 min. giving (1-seleno) – vinyl alkynyl ketones **5** in fair to good yields. (**Table 1**)



Scheme 1

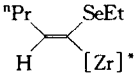
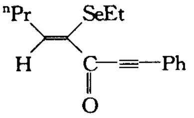
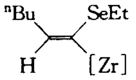
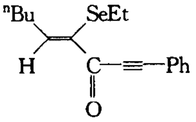
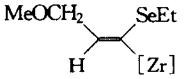
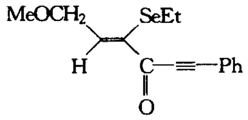
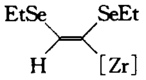
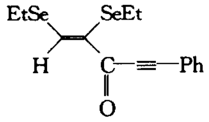
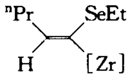
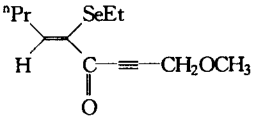
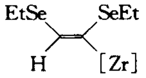
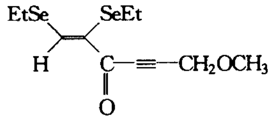
The generation of very reactive acylmetals in which the metal species is a main group metal is a very attractive field ,[9] their usage as an " unmasked " acyl anion for organic synthesis is limited due to their instability . The transition metal acyl complexes have also long attacted much attention because of their intrinsic usefulness as an acyl anion equivalent in organic synthesis.[10] Since the ethylseleno and the zirconocene

PII: S0040-4020(99)00813-3

functions exert an opposing polarization on the olefinic bond, [8a,11] (Z)-α-selenylvinylacylzirconocene chloride **3** represents the synthetic equivalent of the cation-anion synthon **6**. (**Scheme 1**)

We had also tried the coupling of **3c** with haloalkynes in the presence of CuI, but the result was not satisfactory. The reaction needed long time and the yields were low.

Table 1 Copper-catalyzed carbonylative coupling of (E)-α-selanylvinylzirconium with alkynyliodonium tosylates

Entry	(E)-α-Selanylvinyl-zirconium	Alkynyliodoniun	Vinyl alkynyl ketone	Yield[a] (%)
5a		$Ph-\equiv-\overset{+}{I}Ph\,\overset{-}{O}Ts$		80
5b		$Ph-\equiv-\overset{+}{I}Ph\,\overset{-}{O}Ts$		82
5c		$Ph-\equiv-\overset{+}{I}Ph\,\overset{-}{O}Ts$		90
5d		$Ph-\equiv-\overset{+}{I}Ph\,\overset{-}{O}Ts$		85
5e		$CH_3OCH_2-\equiv-\overset{+}{I}Ph\,\overset{-}{O}Ts$		75
5f		$CH_3OCH_2-\equiv-\overset{+}{I}Ph\,\overset{-}{O}Ts$		78

a Isolated yield [Zr]* = Cp_2ZrCl

In conclusion, copper-catalyzed carbonylative cross-coupling of (E)-α-selanylvinylzirconiums with alkynyliodonium tosylates were achieved under extremely mild conditions. The method described herein may afford a way to synthesize unsymmetrical vinyl alkynyl ketones, which are important intermediates in the synthesis of a wide variety of organic compounds.

Experimental

General remarks ^{1}H NMR spectra were recorded on an AZ-300MHz with TMS as internal standard. Mass spectra were determined using a Finigan 8230 mass spectrometer. IR spectra were obtained in neat capillary cells on a shimadzu IR-408 instrument. The reaction were carried out in pre-dried glassware (150℃, 4h) and cooled under a stream of dry nitrogen. All solvents were dried, deoxygenated and redistilled before use. Acetylenic selenides and alkynylphenyliodonium tosylates were prepared according to the literature methods respectively.[12,13]

General procedure for the synthesis of α-seleno-substituted vinyl alkynyl ketones 5a – f

To a freshly prepared suspension of $Cp_2Zr(H)Cl$(4 mmol) in THF (15 ml) at r.t. was added a solution of acetylenic selenides **1** (3 mmol) in THF (1.25 ml) under nitrogen, the reaction mixture was stirred for about 0.5h. until the precipitate completely disappeared. To the resulting clear green solution was then added CuI (3 mmol × 3%) and alkynyliodonium tosylates **4** (3 mmol) under an atmospheric pressure of CO at r.t., the mixture was stirred for 15 min. at ambient temperature. The reaction mixture was treated with aqueous $NaHCO_3$(15 ml), and extracted with ether (3 × 15 ml). The combined ethereal extracts were washed with saturated sodium chloride solution (2 × 10 ml), dried over $MgSO_4$, and concentrated under reduced pressure to give a crude oil, which was purified by flash column chromatograph (silica gel hexane: EtOAc = 10:1) to give **5a – f**.[14]

5a: Yellow oil. ^{1}H NMR ($CDCl_3$, δppm): 7.10 – 7.50(m,5H,$C_6\underline{H}_5$), 6.20(t,J = 6.9Hz,1H, =$C\underline{H}$), 2.54(q,J = 7.8Hz,2H,$SeC\underline{H}_2$), 1.95 – 2.34(m,2H,$C\underline{H}_2$ =), 1.49(t,J = 7.8Hz,3H,$SeCH_2C\underline{H}_3$), 1.18 – 1.47(m,2H, $C\underline{H}_2$), 0.75(t,J = 5.3Hz,3H,$C\underline{H}_3$). IR ν(cm^{-1}): 3404, 2912, 1600, 1483, 1190, 662. MS: m/z 305(M$^+$). Anal. Calc. for $C_{16}H_{18}SeO$: C, 62.96; H, 5.94%. Found: C, 62.84; H, 6.01%.

5b: Yellow oil. ^{1}H NMR ($CDCl_3$, δppm): 7.12 – 7.53(m,5H,$C_6\underline{H}_5$), 6.19(t,J = 6.8Hz,1H, =$C\underline{H}$), 2.54(q,J = 7.9Hz, 2H, $SeC\underline{H}_2$), 1.96 – 2.35(m,2H,$C\underline{H}_2$ =), 1.48(t,J = 7.9Hz,3H,$SeC\underline{H}_3$), 1.14 – 1.49(m,4H, $C\underline{H}_2C\underline{H}_2$), 0.81(t,J = 5.4Hz,3H,$C\underline{H}_3$). IR ν(cm^{-1}): 3403, 2922, 1609, 1485, 1192, 701. MS: m/z 319 (M$^+$). Anal. Calc. for $C_{17}H_{20}SeO$: C,63.95; H,6.31%. Found: C,63.74; H,6.40%.

5c: Yellow oil. ^{1}H NMR ($CDCl_3$, δppm): 7.10 – 7.49(m,5H,$C_6\underline{H}_5$), 6.30(t,J = 7.0Hz,1H, =$C\underline{H}$), 3.85(d,J = 7.0Hz,2H, =$C\underline{H}_2OCH_3$), 3.25(s,3H,$OC\underline{H}_3$), 2.61(q,J = 7.7Hz,2H,$SeC\underline{H}_2$), 1.39(t,J = 7.7Hz,3H, $SeCH_2C\underline{H}_3$). IR ν(cm^{-1}) 3110, 2925, 1690, 1495, 1201, 700. MS: m/z 307(M$^+$). Anal. Calc. for $C_{15}H_{16}SeO_2$: C,58.64; H,5.25%. Found: C,58.23; H,5.31%.

5d: Yellow oil. ^{1}H NMR ($CDCl_3$, δppm): 7.09 – 7.25(m,5H,$C_6\underline{H}_5$), 6.75(s,1H, =$C\underline{H}$), 2.62(q,J = 7.4Hz, 4H,$SeC\underline{H}_2$), 1.40(t,J = 7.4Hz,6H,$SeCH_2C\underline{H}_3$). IR ν(cm^{-1}): 3420, 2950, 1600, 1420, 1198, 710, 690. MS: m/z 370(M$^+$). Anal. Calc. for $C_{15}H_{16}Se_2O$: C,48.67; H,4.36%. Found: C, 48.45; H,4.54%.

5e: Yellow oil. ^{1}H NMR ($CDCl_3$, δppm): 6.30(t,J = 6.9Hz,1H, =$C\underline{H}$), 3.90(s,2H,$\equiv - C\underline{H}_2OCH_3$), 3.22(s, 3H,$OC\underline{H}_3$), 2.52(q,J = 7.7Hz,2H,$SeC\underline{H}_2$), 1.97 – 2.40(m,2H,$C\underline{H}_2$ =), 1.50(t,J = 7.7Hz,3H,$SeCH_2C\underline{H}_3$), 1.18 – 1.45(m,2H,$C\underline{H_2}$), 0.76(t,J=5.4Hz,3H,$C\underline{H_3}$). IR ν(cm^{-1}): 3410, 2933, 1610. MS: m/z 273(M$^+$). Anal. Calc. for $C_{12}H_{18}SeO_2$: C,52.77; H,6.64%. Found: C,52.43; H,6.82%.

5f: Yellow oil. ^{1}H NMR (CDCl$_3$,δppm): 6.25(s,1H, =$C\underline{H}$), 3.95(s,2H,≡–$C\underline{H_2}OCH_3$), 3.23(s,3H,$OC\underline{H_3}$), 2.65(q,J=7.4Hz,4H,$SeC\underline{H_2}$), 1.42(t,J=7.4Hz,6H,$SeCH_2C\underline{H_3}$). IR ν(cm^{-1}): 3423, 2952, 1603. MS: m/z 338(M$^+$). Anal. Calc. for $C_{11}H_{16}Se_2O_2$: C,39.08; H,4.77%. Found: C,39.32; H,4.59%.

Acknowledgements

Projects 29493800, 29772007 supported by the National Natural Science Foundation of China. This work was also supported by the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Academia Sinica.

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14. Compound 5a – f were unstable. We found the compounds began to decompose at 110℃ under the reduced pressure.