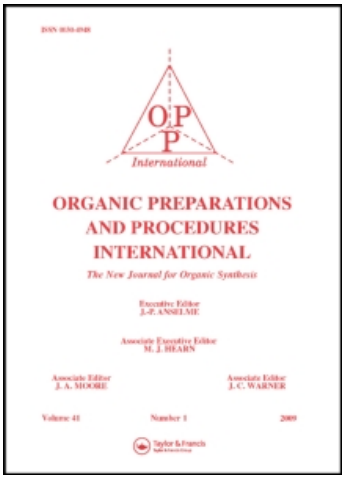

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ONE-POT SYNTHESIS OF SELENOESTERS FROM ALKYNYL ARYL SELENIDES

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12. A NOESY spectrum of the major isomer of **2a** showed no correlation between the methyl and the ethyl ester suggesting the *Z* geometry about the double bond. Further, the chemical shift of the enol proton (δ 13.1) indicated strong hydrogen bonding which is only possible with a *cis* orientation of the enol hydroxy and the ester carbonyl.

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ONE-POT SYNTHESIS OF SELENOESTERS FROM ALKYNYL ARYL SELENIDES

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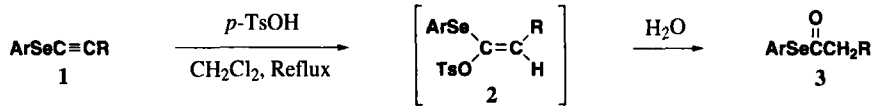
Organoselenium compounds have attracted considerable interest as reagents and intermediates in organic synthesis.[1] Selenoesters, a class of useful intermediates in the synthesis of natural compounds,[2] are commonly prepared by the reaction of acyl halides with selenols,[2,3] or by the alkylation of the selenolate ion.[4] Recently, other methods from arylselenotrimethyl-silane[5] and diselenides[6-8] have also been reported. However, most of these preparations are limited to alkyl esters, or involve difficult removal of by-products such as diaryl diselenides, harsh reaction conditions, laborious manipulation, low yields, or in some cases, reagents are not readily available. Herein, we report a one-pot, two-step synthesis of selenoesters **(3)** from alkynyl aryl selenides **(1),** which are treated succes-

sively with *p*-toluenesulfonic acid[9] and water. The present method has the advantage of ready availability of starting materials, mild reaction condition, convenient manipulation and good (70-80%) yields.



a) Ar = C_6H_5 R = C_6H_5 e) Ar = *p*-$CH_3C_6H_4$ R = C_6H_5
b) Ar = C_6H_5 R = C_2H_5 f) Ar = *p*-$CH_3C_6H_4$ R = *n*-C_4H_9
c) Ar = C_6H_5 R = *n*-C_4H_9 g) Ar = *p*-$CH_3C_6H_4$ R = C_2H_5
d) Ar = C_6H_5 R = *p*-$CH_3C_6H_4$ h) Ar = *o*-$CH_3C_6H_4$ R = CH_3

EXPERIMENTAL SECTION

Mps are uncorrected.^{1}H NMR spectra were recorded on Varian EM-360 and FX–90Q instruments using $CDCl_3$ as the solvent and with TMS as an internal standard. Infrared spectra were obtained on a BIO-RAD FT-40 spectrophotometer. Elemental analyses were performed on a Carlo Erba-1106 instrument. Alkynyl aryl selenides[10] were prepared according to the literature methods.

General Procedure for the Preparation of Selenoesters.- A mixture of the alkynyl aryl selenide (2.0 mmol) [prepared[10] from the reaction of terminal alkynes with iodobenzene diacetate and diphenyl diselenide in methylene chloride at 0°], and *p*-toluenesulfonic acid (1.14g, 6.0 mmol) in methylene chloride (10 mL) was refluxed for 4 h and cooled to room temperature. The mixture was treated with H_2O (1 mL) and stirred overnight at room temperature. It was then neutralized with a saturated solution of K_2CO_3 (15 mL) and washed with a saturated solution of NaCl (15 mL), and extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with water and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* and the crude product was purified by preparative TLC on silica gel (hexane/ethyl acetate (20/1 as eluent).

The ^{1}H NMR spectra of **3b**[8] **3c**[8] **3f**[14] **3g**[15] and **3h**[15] were identical to those reported in the references cited.

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TABLE. Selenoesters from Aryl Alkynyl Selenides[a]

Cmpd	Yield (%)	mp (°C)	*lit.*mp (°C)	IR (cm^{-1}) (CO)	^1H NMR (δ)	Elemental Analysis (Found) C	H
3a	81	42-43	41-42[11]	1695	7.73-7.10 (m,10H); 4.42 (s,2H)	61.10 (61.16)	4.40 (4.45)
3b	73	oil		1735	7.65-7.02 (m,5H); 2.66 (t,2H); 2.06-1.41 (m,2H); 0.95 (t,3H)	52.87 (52.90)	5.33 (5.30)
3c	72	oil		1740	7.60-7.21 (m,5H); 2.60 (t,2H); 1.41-1.12 (m,6H); 0.88 (t,3H)	56.47 (56.58)	6.32 (6.40)
3d	80	69-70	69-70[12]	1690	7.68-7.05 (m,9H); 4.45 (s,2H); 2.23 (s,3H)	62.28 (62.18)	4.88 (4.96)
3e	78	42-43	43[13]	1701	7.54-6.98 (m,9H); 4.47 (s,2H); 2.24 (s,3H)	62.28 (62.20)	4.88 (4.93)
3f	68	oil		1741	7.45-7.00 (m,4H); 2.54 (t,2H); 2.22 (s,3H); 1.44-1.15 (m,6H); 0.86 (t,3H)	57.99 (58.08)	6.74 (6.82)
3g	70	oil		1742	7.32-7.10 (m,4H); 2.60 (t,2H); 2.28 (s,3H); 1.60-1.43 (m,2H); 0.95 (t,3H)	54.78 (54.70)	5.87 (5.93)
3h	71	oil		1744	7.34-7.12 (m,4H); 2.61 (q,2H); 2.30 (s,3H); 1.25-0.98 (t,3H)	52.87 (52.79)	5.33 (5.37)

a) All compounds are light yellow crystals or oils.

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$NaBH_4$-$MnCl_2$ FOR IMPROVED REDUCTION OF β-KETO ESTERS ATTACHED TO A CHIRAL AUXILIARY. COMPARISON WITH $Zn(BH_4)_2$

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The chemo- and stereoselective reduction of β-keto esters is an efficient and useful strategy for the synthesis of biologically active compounds such as natural products,[1] β-lactam antibiotics,[2] fluoxetine[3] and the HR 780,[4] an HMG-CoA reductase inhibitor. In spite of the extensively investigated enantioselective approaches,[5] the use of chiral auxiliaries remains a common and reliable method for the stereoselective reduction of β-keto acids derivatives with hydrides in moderate to high levels of asymmetric induction.[6] Usually these reactions are carried out with $Zn(BH_4)_2$ in the presence of $ZnCl_2$ as the complexing additive of both carbonyls of the β-keto ester **1** in order to prevent carbon-