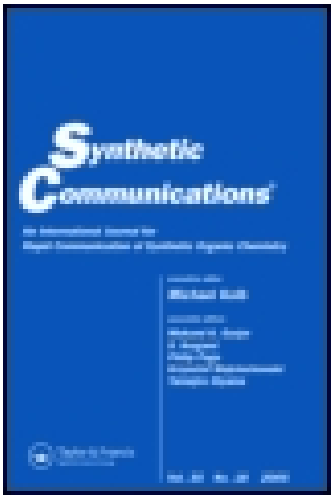

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A Facile Synthetic Route to α-Selenoketones Promoted by SmI_2 OR SmI_3

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A FACILE SYNTHETIC ROUTE TO α-SELENOKETONES PROMOTED BY SmI_2 OR SmI_3

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ABSTRACT: α — Arylseleno or α — alkylselenoketones were synthesized by reactions of α—haloketones with RSeBr mediated by SmI_2 or SmI_3

α—Phenylseleno carbonyl compounds have a wide range of synthetic utilities. They have been used for regioselective introduction of various functional groups, especially for that of unsaturation via well established syn—elimination[1]. A variety of methods are now available for the introduction of phenylseleno group into α—position of the carbonyl compounds. They have been previously prepared from, among others, ketones[1], olefins[2], acetylenes[3], Selenoesters[4] and phenylselenoacetaldehyde[5]. But some of them suffer from some disad-

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vantages and drawbacks. For example, direct selenations of ketones are carried out at catalysis of concentrated sulfuric acid[6]. Samarium diiodide has been extensively utilized for a number of organic synthetic reactions as a powerful one—electron transfer reducing agent in the last decade[7]. Very recently the application of trivalent samarium in organic synthesis is rapidly increasing. For example, We found that in the presence of either SmI_3 or Sm/I_2 α—haloketones are able to condense with aldehydes to give α, β—unsaturated ketones[8], 1—chloro—2—heptanone could react with benzaldehyde to form α—chloro—β—hydroxy ketones promoted by $Sm(HMDS)_3$[9]; catalyzed by $Sm(OTf)_3$ and s—BuLi, methyl—iodide can add to carbonyl group of acetophenone[10]; Mori reported that mediated by SmI_2 or SmI_3 α—haloketones may react with α—ketocarboxylates and α—diketones to give α—hydroxy—γ—ketocarboxylates and 2—hydroxy—1, 4—diketones respectively[11]. In this communication we wish to report that samarium enolates formed in situ from α—haloketones can react with RSeBr to give arylseleno or alkylseleno ketones.

$$ArCOCH_2Br + RSeBr \xrightarrow[CH_3CN]{SmI_2 \text{ or } SmI_3} ArCOCH_2SeR$$

Ar = Ph, p—ClC_6H_4, p—BrC_6H_4

R = Ph, p—$CH_3C_6H_4$, $CH_3CH_2CH(CH_3)$—

The reactions occur at room temperatures and neutral, mild conditions with good yields. It is apparent from Table that the reaction times with SmI_2 are shorter than that with SmI_3, but their yields differences are comparatively small.

Table. Reaction Times and Yields

NO.	α—Seleno Ketones	SmI_2		SmI_3	
		Reaction Times (h)	Yields (%)	Reaction Times (h)	Yields (%)
1	$PhCOCH_2SePh$	2	66	3	70
2	$PhCOCH_2SeCH(CH_3)CH_2CH_3$	2	76	3	73
3	$PhCOCH_2SeC_6H_4CH_3$-p	2	72	3	69
4	p—$ClC_6H_4COCH_2SePh$	2	66	3	70
5	p—$ClC_6H_4COCH_2SeCH(CH_3)CH_2CH_3$	2	69	3	75
6	p—$ClC_6H_4COCH_2SeC_6H_4CH_3$—p	2	59	3	64
7	p—$BrC_6H_4COCH_2SePh$	2	67	3	70
8	p—$BrC_6H_4COCH_2SeCH(CH_3)CH_2CH_3$	2	69	3	72
9	p—$BrC_6H_4COCH_2SeC_6H_4CH_3$—p	2	58	3	61

Experimental

Proton NMR spectra were recorded in CCl_4 on JEOL PMX 60si spectrometer using TMS as internal standard. IR spectra were obtained on a PE 683 instrument. Mass spectra were recorded on a HP 5989A mass spectrometer.

The solvents were predried according to standard procedures before use. The reactions were performed in a Schlenk type glass apparatus and under a nitrogen atmosphere.

General Procedure For The Preparations of α—Selenoketones with SmI_2: After α-haloketone (1mmol, in 2 ml CH_3CN) was added to SmI_2(2.1 mmol, in 20ml CH_3CN) the solution turned to yellow—brown immediately. Then RSeBr(1.1 mmol, in 4 ml CH_3CN) was added to the solution and let them react for 1h. Dilute hydrochloric acid (o.1M, 1 ml) was dropped into the reaction mixture. Before the mixture was extracted with ether, some of the solvents were evaporated in vacuum. After usual work—up the product was separated by preparative TLC (silica gel) with petroleum ether and ethyl ether (100 : 2) as eluent.

General Procedure For The Preparation of α—Selenoketones Using SmI_3: The sequence of additions of α—haloketone (1mmol, in 2ml CH_3CN) and RSeBr (1.2 mmol, in 2ml CH_3CN) to SmI_3 (1mmol, in 12ml CH_3CN) is arbitrary. The treatment thereafter are the same with above.

2—Phenylseleno acetophenone: oil; ^1H—NMR: 3.93(s,2H), 7.02—7.47(m,8H), 7.65—7.80(m,2H), IR: 1685cm^{-1}; MS (m/e): 275(M^+).

2—(4—Methylphenyl) seleno acetophenone: oil; ^{1}H—NMR: 2.22(s, 3H), 3.90(s, 2H), 6.90, 7.02(d, 2H), 7.27—7.40 (m, 5H), 7.72—7.87 (m, 2H); IR: 1680cm^{-1};MS(m/e): 289 (m^+).

2—(Sec—butyl)seleno acetophenone: oil; ^{1}H—NMR: 0.83, 0.94, 1.05(t,3H), 1.33, 1.43(d,3H), 1.23—1.73(m,2H), 2.78—3.20(m, 1H), 3.60(s,2H), 7.32—7.46(m,3H), 7.78—7.93 (m, 2H); IR: 1680cm^{-1}; MS(m/e): 255(M^+).

2—Phenylseleno—4′—chloroacetophenone: oil; ^{1}H—NMR: 3.90(s,2H),7.07—7.37(m,7H), 7.56—7.82(m, 2H), IR: 1685cm^{-1}; MS(m/e): 309(M^+).

2—(4—Methylphenyl) seleno—4′—chloroacetophenone: m.p.: 95—97℃; ^{1}H—NMR: 2.33(s,3H), 3.92(s,2H), 7.00—7.40(m,6H), 7.57—7.76(m,2H), IR: 1680cm^{-1};MS(m/e): 323(M^+).

2—(Sec—butyl)seleno—4′—chloroacetophenone: oil; ^{1}H—NMR: 0.80, 0.91, 1.03(t,3H), 1.30, 1.41(d,3H), 1.21—1.70(m,2H), 2.73—3.2(m,1H), 3.57(s,2H), 7.27, 7.41, 7.75, 7.90(q,4H); IR:1685cm^{-1}; MS(m/e): 289(M^+).

2—Phenylseleno—4′—bromoacetophenone: oil; ^{1}H—NMR: 3.90(s,2H), 7.05—7.67(m,9H); IR: 1685cm^{-1};MS(m/e); 353(M^+).

2—(4—Methylphenyl) seleno—4′—bromoacetophenone: m.p. 105—107℃. ^{1}H—NMR: 2.26(s,3H), 3.87(s,2H), 6.90, 7.03 (d,2H), 7.23—7.73(m,6H); IR: 1680cm^{-1}; MS(m/e): 367 (M^+).

2—(Sec—butyl)seleno—4′—bromoacetophenone: oil; ^{1}H—NMR: 0.77, 0.88, 1.00(t,3H), 1.27, 1.38(d,3H), 1.18—1.69(m,2H), 2.72—3.14(m,1H), 3.55(s,2H), 7.38, 7.53, 7.65, 7.80(q,4H), IR:1680cm^{-1}; MS(m/e):333(M^+).

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