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A FACILE SYNTHETIC ROUTE TO α-SELENOKETONES PROMOTED BY SmI₂ OR SmI₃

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ABSTRACT: α — Arylseleno or α — alkylselenoketones were synthesized by reactions of α —haloketones with RSeBr mediated by SmI₂ or SmI₃

 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—elimination¹. 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, ketones¹, olefins², acetylenes³, Selenoesters⁴ and phenylselenoacetaldehyde⁵. 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 acid⁶. Samarium diiodide has been extensively utilized for a number of organic synthetic reactions as a powerful one-electron transfer reducing agent in the last decade⁷. 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 $Sm/I_2 \alpha$ - haloketones are able to condense with aldehydes to give α , β — unsaturated ketones⁸, 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 acetophenone¹⁰; Mori reported that mediated by SmI_2 or $SmI_3 \alpha$ haloketones may react with α -ketocarboxylates and α -diketones to give α -hydroxy- γ -ketocarboxylates and 2-hydroxy -1, 4 – diketones respectively¹¹. 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.

ArCOCH₂Br+RSeBr $\xrightarrow{\text{SmI}_2 \text{ or SmI}_3}$ ArCOCH₂SeR

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.

NO.	a-Seleno Ketones	SmI2		SmI3	
		Reaction Times(h)	Yields (%)	Reaction Times(h)	Yields (%)
1	PhCOCH₂SePh	2	66	3	70
2	PhCOCH2SeCHCH2CH3 CH3	2	76	3	73
3	PhCOCH₂SeC₅H₄CH₃.—p	2	72	3	69
4	p—ClC ₆ H ₄ COCH ₂ SePh	2	66	3	70
5	p—CIC6H4COCH2SeCHCH2CH3 CH3	2	69	3	75
6	p-ClC ₆ H ₄ COCH ₂ SeC ₆ H ₄ CH ₃ -p	2	59	3	64
7	p−BrC ₆ H ₄ COCH ₂ SePh	2	67	3	70
8	p—BrC6H4COCH2SeCHCH2CH3 CH3	2	69	3	72
9	p—BrC ₆ H ₄ COCH ₂ SeC ₆ H ₄ CH ₃ —p	2	58	3	61

	Table.	Reaction	Times	and	Yields	
-						

Experimental

Proton NMR spectra were recorded in CCl₄ 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 SmI₂: After α -haloketone (lmmol, in 2 ml CH₃CN) was added to SmI₂(2.1 mmol, in 20ml CH₃CN) the solution turned to yellow-brown immediately. Then RSeBr(1.1 mmol, in 4 ml CH₃CN) was added to the solution and let them react for lh. 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 SmI₃: The sequence of additions of α —haloketone (lmmol, in 2ml CH₃CN) and RSeBr (1.2 mmol, in 2ml CH₃CN) to SmI₃ (lmmol, in 12ml CH₃CN) 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.: $95-97^{\circ}$; ¹H – 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°C. ¹H-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⁺). Acknowledgment: We thank the National Natural Science Foundation of China and Acadenia Sinica for financial supports.

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