

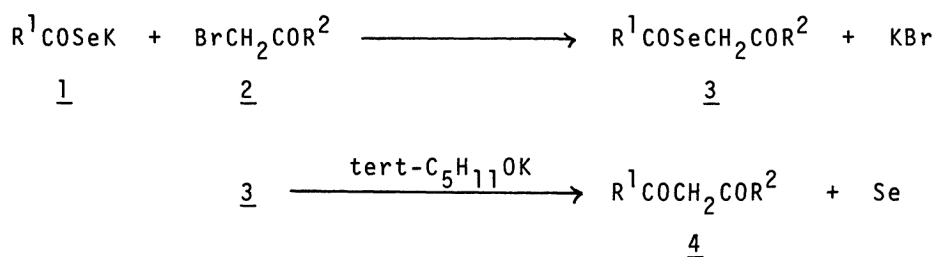
A SYNTHESIS OF 1,3-DIKETONES BY ELIMINATION OF SELENIUM
FROM Se-ACYLMETHYL SELENOCARBOXYLATES

Hideharu ISHIHARA and Yoshio HIRABAYASHI

Faculty of Engineering, Gifu University, Nakamonzencho, Kakamihara, Gifu 504

Se-Acylmethyl selenocarboxylates, prepared by a reaction of potassium selenocarboxylates with α -bromoketones, readily extruded elemental selenium by a treatment with potassium tert-pentoxide to form 1,3-diketones in good yields.

Recently, selenobenzoic acid was obtained by Jensen et al.¹⁾ however, it was very unstable oil. In previous report,²⁾ we described that potassium selenocarboxylates (stable in dry nitrogen), prepared in good yields by a treatment of diacyl selenides with methanolic potassium hydroxide³⁾, were useful as starting material for preparations of selenocarboxylic acid derivatives. In this paper, we wish to report that Se-acylmethyl selenocarboxylates(3), prepared in good yields from potassium selenocarboxylates(1) and α -bromoketones(2), were easily converted to 1,3-diketones by a treatment of potassium tert-pentoxide at room temperature.



Durst⁴⁾ described that acylmethyl carboxylates such as phenacyl carboxylates were conveniently prepared by a reaction of metal carboxylates with α -haloketones in the presence of crown ether as solubilizing catalyst. On the other hand, the reaction of potassium selenocarboxylates with α -bromoketones without catalyst readily afforded the corresponding selenoesters(3) in good yields at room

Table 1 The preparation of Se-acylmethyl selenocarboxylates

	Compound <u>3</u>	Yield %	Mp °C	IR, cm^{-1}	
				$\nu_{\text{C=O}}$	$\nu_{\text{C-Se}}$
a	$\text{C}_6\text{H}_5\text{COSeCH}_2\text{COC}_6\text{H}_5$	93	61.5 - 62.0	1680, 1668	894
b	$p\text{-ClC}_6\text{H}_4\text{COSeCH}_2\text{COC}_6\text{H}_5$	81	89.3 - 90.0	1685, 1665	892
c	$\text{C}_6\text{H}_5\text{COSeCH}_2\text{C}_6\text{H}_4\text{CH}_3(p)$	84	69.3 - 69.7	1690, 1665	890
d	$p\text{-CH}_3\text{OC}_6\text{H}_4\text{COSeCH}_2\text{COC}_6\text{H}_5$	83	77.0 - 77.5	1685, 1662	895
e	$n\text{-C}_{17}\text{H}_{35}\text{COSeCH}_2\text{COC}_6\text{H}_4\text{CH}_3(p)$	88	51.5 - 52.5	1716, 1682	940
f	$\text{C}_6\text{H}_5\text{COSeCH}_2\text{COCH}_3$	80	a)	1708, 1664	880
g	$\text{C}_6\text{H}_5\text{COSeCH}_2\text{COOC}_2\text{H}_5$	77	a)	1732, 1678	887

a) liquid

temperature. For example, a reaction of potassium selenobenzoate(1.12g, 5.0mmol) with α -bromoacetophenone(1.00g, 5.0mmol) in dry ether(20 ml) at room temperature for 2 hr gave Se-benzoylmethyl selenobenzoate(3a)(1.41g, 93%); IR spectrum(KBr disk) $\nu_{\text{C=O}}$ 1668, 1680 cm^{-1} , $\nu_{\text{C-Se}}$ 894 cm^{-1} , NMR spectrum(CCl_4) 7.1-7.5, 7.7-8.1(10H), 4.43 ppm(s, 2H), and elemental analyses; C 58.65, H 4.02, Se 25.58% (Calcd. for $\text{C}_{15}\text{H}_{12}\text{O}_2\text{Se}$: C 59.42, H 3.99, Se 26.04%).

Similarly several selenoesters(3) were readily prepared in good yields as shown in Table 1.

The selenoesters(3) were easily converted to 1,3-diketones with elimination of elemental selenium by a treatment with potassium pentoxide at room temperature. That is, to the solution of Se benzoylmethyl selenobenzoate(0.91g, 3.0 mmol) in dry benzene was added an equimolar amount of potassium tert-pentoxide in tert-pentyl alcohol (2N). The mixture was stirred for 4 hr at room temperature. After the resulting precipitate(elemental selenium, 0.24g, quant.) was filtered off, the filtrate was washed by a cold hydrochloric acid(5%) and water, and dried. The crude product was chromatographed and dibenzoyl methane(0.56g, 83%) was isolated; mp 77 - 78°C, IR spectrum(KBr disk) $\nu_{\text{C=O}}$ 1520 cm^{-1} , NMR spectrum(CCl_4) 6.80(s, 1H), 7.3-7.6, 7.8-8.1 (10H), 16.85ppm(b, 1H).

Similarly several 1,3-diketones(4) were readily obtained in good yields as

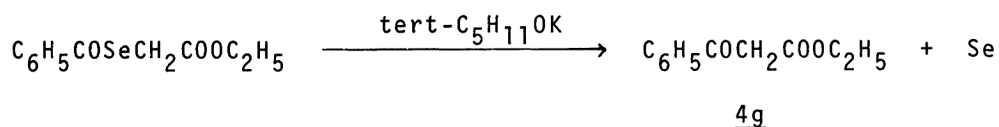
Table 2 The preparation of 1,3-diketones

	Compound	Yield	Mp (lit.)
	<u>4</u>	%	°C
a	$\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5$	83	77 - 78 (77 - 78) ⁵⁾
b	$p\text{-ClC}_6\text{H}_4\text{COCH}_2\text{COC}_6\text{H}_5$	77	86 - 88 (89) ⁶⁾
c	$\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_4\text{CH}_3(p)$	86	83 - 84 (84 - 85) ⁷⁾
d	$p\text{-CH}_3\text{OC}_6\text{H}_4\text{COCH}_2\text{COC}_6\text{H}_5$	80	130 - 131 (130-131) ⁷⁾
e	$n\text{-C}_{17}\text{H}_{35}\text{COCH}_2\text{COC}_6\text{H}_4\text{CH}_3(p)$	70	70 - 71
f	$\text{C}_6\text{H}_5\text{COCH}_2\text{COCH}_3$	46	57 - 59 (60 - 61) ⁸⁾
g	$\text{C}_6\text{H}_5\text{COCH}_2\text{COCOC}_2\text{H}_5$	65	a)

a) liquid

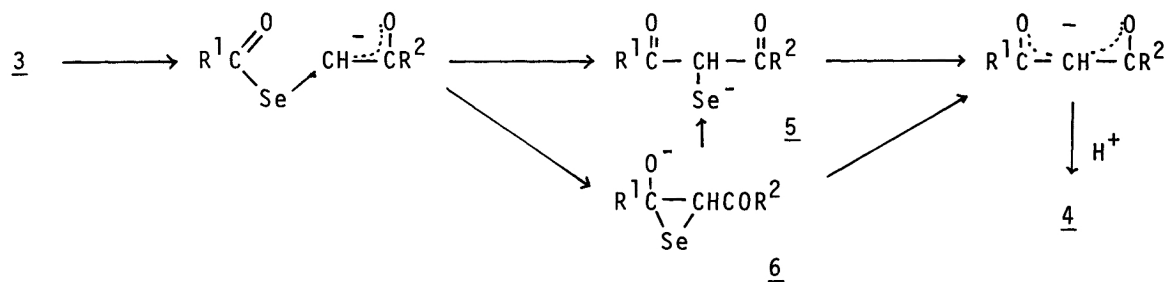
shown in Table 2.

β -ketoester(4g) was, also, prepared in a good yield from the corresponding selenoester and potassium tert-pentoxide in tert-pentyl alcohol; IR spectrum(KBr disk) $\nu_{\text{C=O}}$ 1715, 1683 cm^{-1} , NMR spectrum(CCl_4) 1.21(t, 3H), 3.28(s, 2H), 4.11(q, 2H), 7.2-7.6, 8.0-8.2ppm(m, 5H) and 6.05 and 12.45ppm(enol form).



Eschenmoser et al.⁹⁾ had shown that S-acylmethyl thiocarboxylates were converted to 1,3-diketones by desulfurization with trivalent phosphine in the presence of lithium salts or potassium tert-pentoxide at 50-80°C. In contrast with the thioesters, Se-acylmethyl selenocarboxylates(3) were easily converted by tert-pentoxide to 1,3-diketones without phosphine at mild conditions.

This reaction¹⁰⁾ may be initiated by an attack of tert-pentoxide anion to active methylene, and the resulting enolate anion may cause intramolecular attack on carbonyl carbon, and then elimination of selenium from the resulting intermediate(5 or 6) give 1,3-diketone as shown following scheme.



References and Notes

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(Received June 14, 1978)