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

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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 hydroxide[3], were useful as starting material for preparations of selenocarboxylic acid derivertives. 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.

$$\underset{\underline{1}}{R^1COSeK} + \underset{\underline{2}}{BrCH_2COR^2} \longrightarrow \underset{\underline{3}}{R^1COSeCH_2COR^2} + KBr$$

$$\underline{3} \xrightarrow{\text{tert-}C_5H_{11}OK} \underset{\underline{4}}{R^1COCH_2COR^2} + Se$$

Durst[4] 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 3	Yield %	Mp °C	IR, cm^{-1} νC=O	νC-Se
a	$C_6H_5COSeCH_2COC_6H_5$	93	61.5 - 62.0	1680, 1668	894
b	p-$ClC_6H_4COSeCH_2COC_6H_5$	81	89.3 - 90.0	1685, 1665	892
c	$C_6H_5COSeCH_2C_6H_4CH_3$(p)	84	69.3 - 69.7	1690, 1665	890
d	p-$CH_3OC_6H_4COSeCH_2COC_6H_5$	83	77.0 - 77.5	1685, 1662	895
e	n-$C_{17}H_{35}COSeCH_2COC_6H_4CH_3$(p)	88	51.5 - 52.5	1716, 1682	940
f	$C_6H_5COSeCH_2COCH_3$	80	a)	1708, 1664	880
g	$C_6H_5COSeCH_2COOC_2H_5$	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 gaves Se-benzoylmethyl selenobenzoate(3a)(1.41g, 93%); IR spectrum(KBr disk) νC=O 1668, 1680 cm^{-1}, νC-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 $C_{15}H_{12}O_2Se$: 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 temperatere. 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) νC=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 4	Yield %	Mp (lit.) °C
a	$C_6H_5COCH_2COC_6H_5$	83	77 - 78 (77 - 78)[5]
b	p-$ClC_6H_4COCH_2COC_6H_5$	77	86 - 88 (89)[6]
c	$C_6H_5COCH_2COC_6H_4CH_3$(p)	86	83 - 84 (84 - 85)[7]
d	p-$CH_3OC_6H_4COCH_2COC_6H_5$	80	130 -131 (130-131)[7]
e	n-$C_{17}H_{35}COCH_2COC_6H_4CH_3$(p)	70	70 - 71
f	$C_6H_5COCH_2COCH_3$	46	57 - 59 (60 - 61)[8]
g	$C_6H_5COCH_2COOC_2H_5$	65	a)

a) liquid

shown in Table 2.

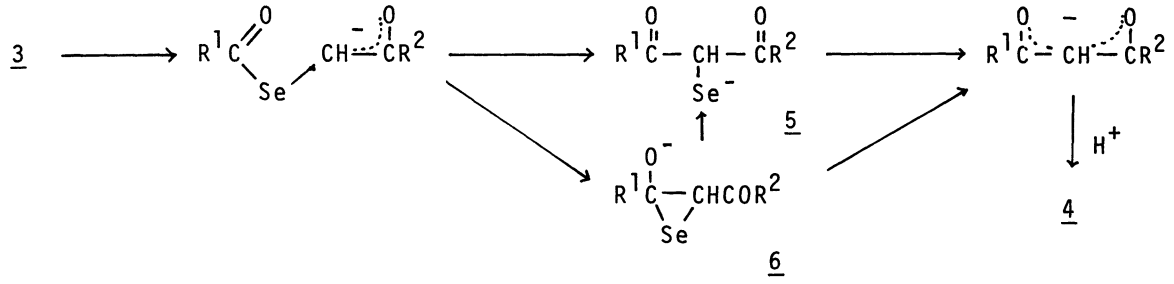
β-ketoester(4g) was, also, prepared in a good yield from the corresponding selenoester and potassium tert-pentoxide in tert-pentyl alcohol; IR spectrum(KBr disk) νC=O 1715, 1683 cm^{-1}, NMR spectrum(CCl_4) 1.21(t, 3H), 3.28(s, 2H), 4.11(q, 2H), 7.2-7.6, 8.0-8.2ppm(m, 5H) and 6.05 and 12.45ppm(enol form).

$$C_6H_5COSeCH_2COOC_2H_5 \xrightarrow{\text{tert-}C_5H_{11}OK} C_6H_5COCH_2COOC_2H_5 + Se$$

4g

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 reaction[10] 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.



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