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SYNTHESIS OF ALKYL PHENYL SELENIDES BY THE REACTION OF PHENYL TRIMETHYLSILYL SELENIDE WITH ACETATES AND LACTONES

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The reaction of phenyl trimethylsilyl selenide with acetates and lactones using zinc iodide gave alkyl phenyl selenides and ω-phenylselenenylcarboxylic acids respectively.

Recently a convenient method for the synthesis of phenyl trimethylsilylselenide(1)[1] has been reported by us[2] and independently by Detty.[3]

$$\mathrm{PhSeSePh} \xrightarrow[\text{2) } Me_3SiCl]{\text{1) Na}} \underset{\underline{1}}{\mathrm{PhSeSiMe_3}}$$

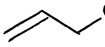
Since the silyl selenide 1 consists of a hard acid (Me_3Si) and a soft base (PhSe), high reactivity of 1 toward oxygenated function (hard base) would be anticipated. The reaction of 1 with ketones, aldehydes and enones has been reported recently.[4] The reagent 1 also serves as a precursor of benzeneselenol[1] as well as of potassium phenyl selenolate, and the latter has been used for ring opening of lactones under slightly basic condition.[3]

These reports have prompted us to disclose our results of the reaction of 1 with alkyl acetates as well as with lactones in the presence of a Lewis acid catalyst (ZnI_2). The reaction provides a new method for the introduction of phenylseleno group to an organic molecule.

$$\mathrm{ROAc} \quad + \quad \underset{\underline{1}}{\mathrm{PhSeSiMe_3}} \xrightarrow{\text{cat. } ZnI_2} \mathrm{RSePh} \quad + \quad \mathrm{Me_3SiOAc}$$

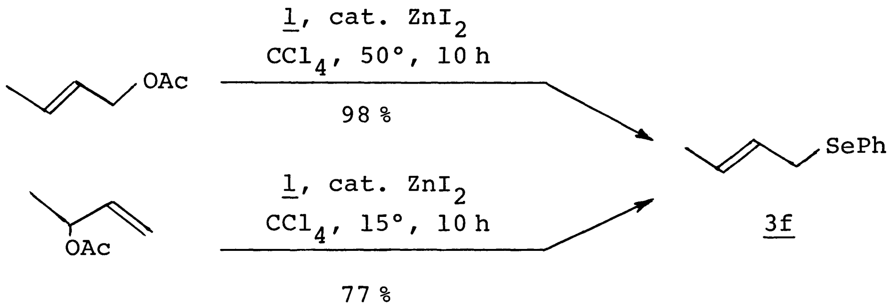
The results from the reaction of various acetates are shown in Table I.[5] Each reaction was carried out using 5 mmol of the acetate, 6 mmol of 1 and a catalytic amount of zinc iodide (16 mg; 0.05 mmol). The reaction was followed by glc up to 20 h and the time necessary for the complete consumption of the acetate was given in the Table.

Table I Reaction of Phenyl Trimethylsilyl Selenide with Alkyl Acetates[a)]

Acetate	Solvent	Temp (°C)	Time (h)	Alkyl Phenyl Selenide 2	Yield[b)] (%)
n-BuOAc	CCl_4	80	20	2a	no reaction
	toluene	110	20		65
sec-BuOAc	CCl_4	80	20	2b	no reaction
	toluene	110	20		50
t-BuOAc	CCl_4	50	2	2c	67
	toluene	15	5		65
	CH_2Cl_2	15	10		77
$PhCH_2OAc$	CCl_4	50	7	2d	87
OAc	CCl_4	50	7	2e	76

a) Ester (5 mmol), $PhSeSiMe_3$ (6 mmol), ZnI_2 (0.05 mmol).
b) Isolated yield by column chromatography using silica gel.

The higher reactivity of t-BuOAc than that of n-BuOAc and sec-BuOAc is of interest. The similar enhanced reactivity of t-BuOAc[6)] and t-BuOSiMe$_3$[7)] toward Me_3SiI has been reported. Substitutions at the tertiary carbon atom under the influence of the reagents having Lewis acid character have also been observed in the reaction of t-BuCl with mercuric acetate,[8)] trialkylalanes,[9)] and enol silyl ethers.[10)] Although details are not known, cationic transition state seems to be important in these reactions. Thus, in the present reaction, interaction of the silyl selenide 1 with zinc iodide followed by subsequent transfer of the silyl group to the carbonyl oxygen may result in activation of the leaving group in alkyl acetate. Then, the carbon-oxygen bond may cleave in S_N2-like manner for R=n-Bu and sec-Bu, and in S_N1-like manner for R=t-Bu. The observed facile substitution of benzyl and allyl acetates also suggests the importance of cationic transition state. Crotyl acetate and 1-buten-2-yl acetate reacted with 1 to give the same selenide (3f). Whether this allylic selenide is kinetic or thermodynamic product is not known.[11)]



Lactones have also been found to react with the silyl selenide 1 using ZnI_2 as a catalyst. As shown in Table II, some ω-phenylselenenylcarboxylic acids were obtained.[5] For the ease of isolation of the product, the reaction mixture was treated with methanol to give the corresponding acids.

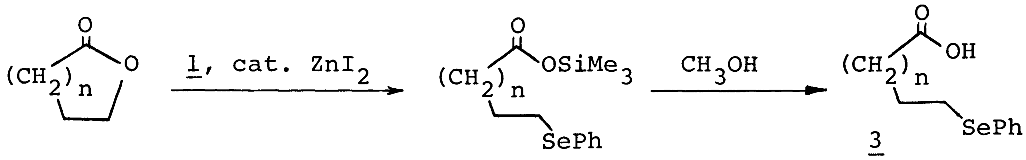
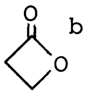
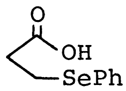
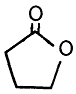
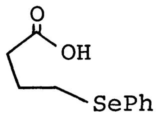
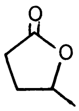
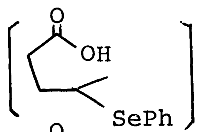
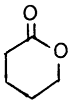
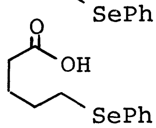
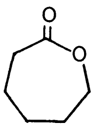
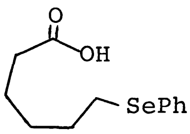


Table II Reaction of Phenyl Trimethylsilyl Selenide with Lactones[a)]

Lactone	Solvent	Temp(°C)	Time(h)	Product(3)		Yield(%)
 b)	CH_3CN	80	5	3a		86
	CH_3CN toluene	80 110	10 20	3b		no reaction 79
	toluene	110	20	3c		no reaction
	toluene	110	20	3d		70
	toluene	110	5	3e		100

a) Lactone(5 mmol), $PhSeSiMe_3$(7.7 mmol), ZnI_2(0.05 mmol).
b) Without use of ZnI_2.

These reactions may provide useful methods of phenylselenenylation of esters and lactones under weakly acidic condition which are complementary to known methods using basic conditions.[12)]

References and Notes

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5) All new compounds are adequately characterized by the standard method. NMR data of the products 2a-f and 3a-e are given below: (2a); δ2.82(t, J= 7Hz, 2H, CH_2SePh). (2b); δ3.16(sextet, J= 6Hz, 1H, CHSePh). (2c); δ1.41(s, 9H, $C(CH_3)_3$). (2d); δ3.95(s, 2H, CH_2SePh). (2e); δ3.38(d, J= 7Hz, 2H, CH_2SePh). (2f); δ3.46(d, J= 6Hz, 2H, CH_2SePh). (3a); δ2.47-3.37 (m, 4H, methylene). (3b); δ2.50(t, J= 7Hz, 2H, CH_2C(=O)OH), δ2.95(t, J= 7Hz, 2H, CH_2SePh). (3d); δ2.04-2.42(t, J= 6Hz, 2H, CH_2C(=O)OH), δ2.57-2.87(t, J= 7Hz, 2H, CH_2SePh). (3e); δ2.25(t, J= 6Hz, 2H, CH_2C(=O)OH), δ2.80(t, J= 6Hz, 2H, CH_2SePh).

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