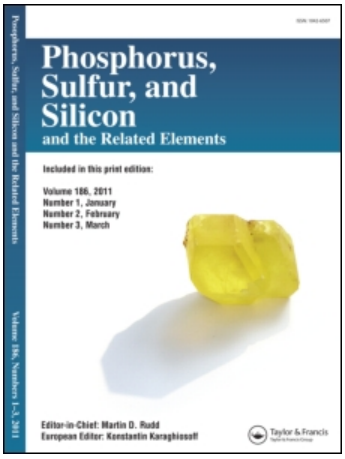

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Synthetic Application of Selenostannanes: Seleno-Alkoxylation of Acetals

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SYNTHETIC APPLICATION OF SELENOSTANNANES: SELENO-ALKOXYLATION OF ACETALS

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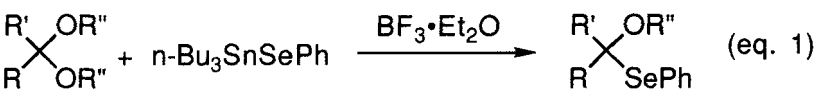
Abstract Monoselenoacetals were easily prepared from the corresponding acetals and tributyltin phenyl selenide (n-$Bu_3SnSePh$) by the action of $BF_3 \cdot Et_2O$ in fair to good yields.

Recently there is increasing interest in the utilization of organoselenium compounds having selenium-metal bond in organic synthesis.[1] However, few studies have been reported concerning the synthetic application of the compounds containing selenium-tin bond such as bis(triphenyltin) or bis(tributyltin) selenide ($(R_3Sn)_2Se$)[2,3] and trialkyltin phenyl selenide ($R_3SnSePh$),[4] probably because of the stability of Se-Sn bond.[5] We found that the Se-Sn bond in tributyltin phenyl selenide (n-$Bu_3SnSePh$) is activated toward acetals under the influence of Lewis acid such as $BF_3 \cdot OEt_2$ (eq. 1).



(eq. 1)

In order to reveal the effect of Lewis acid and solvent, the reaction of dimethoxymethane with n-$Bu_3SnSePh$ was chosen as a model reaction (Table I). The employment of $BF_3 \cdot OEt_2$ was crucial since

Table I. Selenoalkoxylation of Dimethoxy Methane[a)]

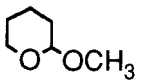
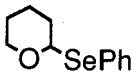
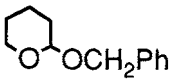
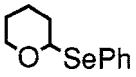
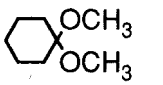
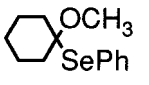
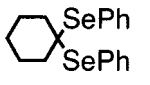
run	Lewis acid	solvent	yield,%[b)]	
			$CH_2(OCH_3)SePh$	$CH_2(SePh)_2$
1	$BF_3 \cdot OEt_2$	$PhCH_3$	100(71)	0
2	$BF_3 \cdot OEt_2$	CH_2Cl_2	56	5
3	$BF_3 \cdot OEt_2$	Et_2O	32	10
4	$BF_3 \cdot OEt_2$	CH_3CN	27	0
5[c)]	$AlCl_3$	CH_2Cl_2	complex mixtures	
6[c)]	$TiCl_4$	CH_2Cl_2	12	22
7[c)]	$SnCl_4$	CH_2Cl_2	14	11

a) Reaction conditions: $CH_2(OCH_3)_2$ (1 mmol), n-$Bu_3SnSePh$ (1.1 mmol), Lewis acid (1.2 mmol), solvent (5 mL), 20°C, 3 h.
b) GLC yields. Number in parentheses is the isoleted yield.
d) -25°C, 3 h.

the yields and the selectivities for monoselenoacetals over diselenoacetals were lowered when Lewis acids such as $AlCl_3$, $TiCl_4$, and $SnCl_4$, were used (runs 1 and 5-7). Toluene was the best solvent for this transformation (run 1). Use of dichloromethane, ether, and acetonitrile as a solvent gave the less satisfactory results (runs 2-4).

The results obtained for a wide variety of acetals are shown in Table II.[6)] Acetals derived from aliphatic aldehydes were converted into the corresponding monoselenoacetals in moderate to good yields, whereas benzaldehyde dimethylacetal produced diselenoacetal,

Table II. Synthesis of Monoselenoacetals

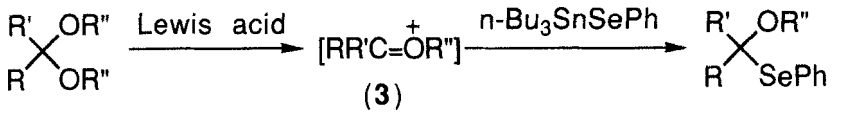
run	acetal	products(yield, %)[a, b]		
1	$CH_2(OCH_3)_2$	$CH_2(OCH_3)SePh$ (71)		
2	$CH_2(OC_2H_5)_2$	$CH_2(OC_2H_5)SePh$ (76)		
3[c]	$CH_2(OC_2H_5)_2$	$CH_2(OC_2H_5)SeC_4H_9$ (76)		
4[d]	$CH_3CH(OCH_3)_2$	$CH_3CH(OCH_3)SePh$ (44)		
5[d]	$C_7H_{15}CH(OCH_3)_2$	$C_7H_{15}CH(OCH_3)SePh$ (50)		
6	$PhCH(OCH_3)_2$	$PhCH(OCH_3)SePh$ (12)	$PhCH(SePh)_2$ (43)	
7[d]		 (42)	$HOC_4H_8CH(OCH_3)SePh$ (20)	
8[d]		 (39)	$HOC_4H_8CH(OCH_2Ph)SePh$ (33)	
9	$C_6H_{13}OCH_2OCH_3$	$C_6H_{13}OCH_2SePh$ (50)	$PhSeCH_2OCH_3$ (13)	
10[e]		 (42)		(13)

a) Isolated yields. b) Based on acetals. c) $Bu_3SnSeBu$ was used. d) -20 °C, 3h. e) -78 °C, 3 h.

$PhCH(SePh)_2$ (43 %), in preference to monoselenoacetal (12 %) (runs 1-7 and 10). Similarly, $Bu_3SnSeBu$ served as a selenolate agent (run 3). The reaction proceeded with cyclic ethers having α-alkoxy substituent (runs 7 and 8). Of special interest is that methoxymethyl (MOM) ether are converted into the corresponding phenylselenomethyl ether in good selectivity (run 9).

Although the mechanism of this selenoalkoxylation is not fully understood, the course of the reaction may be suggested as Scheme I. Acetal is attacked by Lewis acid to form an oxonium ion (**3**), on which subsequent reaction with n-$Bu_3SnSePh$ gives the corresponding monoselenoacetal.

Scheme I. A Possible Reaction Path



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1) For example: a) S. Patai, The Chemistry of Organic Selenium and Tellurium Compounds, edited by Z. Rappoport (Wiley, New York, Vol 1, 1986) b) The Chemistry of Organic Selenium and Tellurium Compounds, edited by S. Patai (Wiley: New York, Vol 2, 1987). c) C. Paulmier, Organic Chemistry Series: Selenium Reagents and Intermediates in Organic Synthesis (Pergamon Press Vol 4, 1986). d) Organoselenium Chemistry, edited by D. Liotta, (Wiley, 1987).
2) D. N. Harpp and M. Gingras, J. Am. Chem. Soc., 110, 7737 (1988).
3) M. Segi, A. Kojima, T. Nakajima, S. Suga, Synlett, 105 (1991).
4) E. W. Abel, B. C. Crosse, and G. V. Hutson, J. Chem. Soc. (A), 2014 (1967).
5) The bond energy of Sn-Se bond is D^0_{298}=98.2 ± 3 kcal/mol in: K. C. Mills, Thermodynamic Data for Inorganic Sulfides, Selenides, and Tellurides (Redwood Press, England, 1974), p 594.
6) Typical Procedure: To a toluene solution of $CH_2(OCH_3)_2$ (1 mmol) and n-$Bu_3SnSePh$ (1.1 mmol) was added BF_3•OEt_2 (1.2 mmol) at 0°C. The solution was stirred at 20 °C for 3 h. Dry pyridine (0.24 mL) and 1M NaOH solution (20 mL) were added to the reaction mixture, which, then, was diluted with ether (30 mL). The organic layer was washed with 1M NaOH solution (20 mL) and water (20 mL). The extracts were dried over Na_2SO_4. Evaporation of the solvent and purification by column chromatography on silica gel gave $CH_2(OCH_3)SePh$ in 71 % yield.