

Selective Synthesis of 1-Alkoxy-3-phenylseleno-1-alkenes and 3-Phenylselenoalkanal by the Reaction of Diisobutylaluminum Phenylselenolate with α,β -Unsaturated Acetals

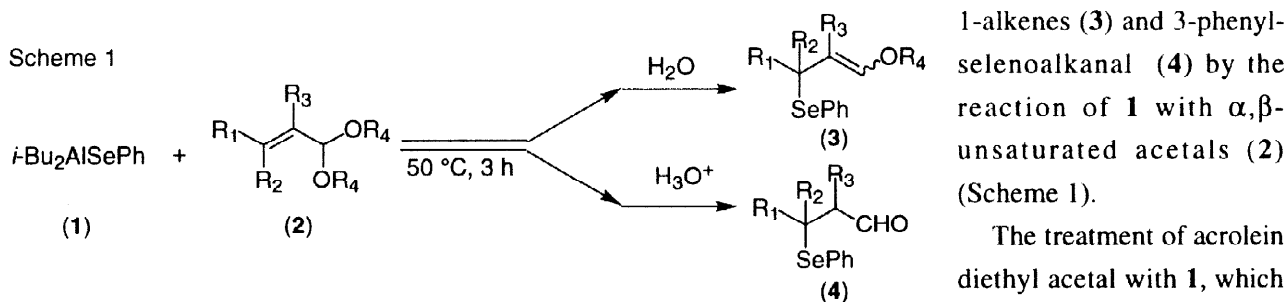
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Abstract: The reaction of α,β -unsaturated acetals with diisobutylaluminum phenylselenolate followed by treatment with H_2O affords the corresponding 1-alkoxy-3-phenylseleno-1-alkenes in good yields. When aq. HCl instead of H_2O was employed in the workup, 3-phenylselenoalkanal were formed in good yields.
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The chemistry of organoselenium compounds having a selenium-metal bond is of great importance and interest.¹⁾ Recently, the utilization of organoselenium compounds bearing various selenium-metal bonds was attempted in organic synthesis and these reagents were recognized as useful for the introduction of the alkyl- or phenylseleno function into various compounds and for the reduction of various organic compounds.²⁻⁴⁾ In our preliminary report, we disclosed a synthetic method of monoselenoacetals by the reaction of acetals with diisobutylaluminum phenylselenolate (*i*-Bu₂AlSePh) (**1**).^{2c)} In the course of our study on the development of new synthetic reactions using **1**, we have now found a selective synthetic method of 1-alkoxy-3-phenylseleno-



1-alkenes (**3**) and 3-phenylselenoalkanal (**4**) by the reaction of **1** with α,β -unsaturated acetals (**2**) (Scheme 1).

The treatment of acrolein diethyl acetal with **1**, which was generated *in situ* from diphenyl diselenide and *i*-Bu₂AlH, in toluene solution at $50\text{ }^\circ\text{C}$ for 3 h produced 1-ethoxy-3-phenylseleno-1-propene in 80 % yield with a mixture of stereoisomers (*E:Z* = 80:20) (entry 1 in Table 1).^{5,6)} This reaction exhibits high regioselectivity and 1-ethoxy-1-phenylseleno-3-propene was not isolated at all.⁷⁾ As well as acrolein diethyl acetal, α,β -unsaturated acetals, which have an internal carbon-carbon double bond, gave the corresponding 1-alkoxy-3-phenylseleno-1-alkenes in good yields (entries 2, 4 and 5). Dimethylacetals shows the same reactivity as that of the diethyl derivative (entry 6). In the case of cinnamaldehyde diethyl acetal, the yield of product was decreased (entry 7). In this reaction, 3-methylbutenal and geranal diethyl acetal derived from the β,β -dialkylsubstituted α,β -unsaturated aldehydes, were also converted into the corresponding 1-alkoxy-

Table 1. Selective Synthesis of 1-Alkoxy-3-phenylseleno-1-alkenes and 3-Phenylselenoalkanal

Entry	Substrate	Yield / % (<i>E</i> / <i>Z</i>) ^{a,b}	
		3	4
1	R ₁ = R ₂ = R ₃ = H, R ₄ = C ₂ H ₅	80 (80 / 20)	78
2	R ₁ = CH ₃ , R ₂ = R ₃ = H, R ₄ = C ₂ H ₅	82 (90 / 10)	80
3	R ₁ = R ₂ = CH ₃ , R ₃ = H, R ₄ = C ₂ H ₅	79 (64 / 36)	76
4	R ₁ = C ₂ H ₅ , R ₂ = R ₃ = H, R ₄ = C ₂ H ₅	75 (68 / 32)	75
5	R ₁ = C ₃ H ₇ , R ₂ = R ₃ = H, R ₄ = C ₂ H ₅	84 (73 / 27)	82
6	R ₁ = C ₃ H ₇ , R ₂ = R ₃ = H, R ₄ = CH ₃	84 (76 / 24)	81
7	R ₁ = C ₆ H ₅ , R ₂ = R ₃ = H, R ₄ = C ₂ H ₅	35 (83 / 17)	32
8	R ₁ = (CH ₃) ₂ C=CHCH ₂ CH ₂ , R ₂ = CH ₃ , R ₃ = H, R ₄ = C ₂ H ₅	76 (72 / 28)	72

a) Isolated yields. b) The ratio of *E* and *Z* was determined by ¹H NMR.

In summary, the selective syntheses of 1-alkoxy-3-phenylseleno-1-alkenes and 3-phenylselenoalkanal based on the reaction of α,β -unsaturated acetals with *i*-Bu₂AlSePh have been developed. Further investigations along these lines are now in progress.

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- 4) For examples of organic syntheses using selenium compounds having Se-Sn bond; Y. Nishiyama, H. Ohashi, K. Itoh, N. Sonoda, *Chem. Lett.* **1998**, 115 and references cited therein.
- 5) To a toluene (5 ml) solution of PhSeSePh (0.5 mmol) was added a small excess amount of a 1.5 M toluene solution of *i*-Bu₂AlH (1.2 mmol) at 0°C and the solution was stirred at that temperature for 30 min. α,β -Unsaturated acetal (1.2 mmol) was added to the resulting solution and stirred at 50 °C for 4 h. After the reaction, H₂O or 1M HCl (15 mL) was added to the reaction mixture, extracted with diethyl ether (20 mL x 3) and dried over MgSO₄. The solvent was removed under reduced pressure, and the resulting oil was isolated by column chromatography on silica gel to give the corresponding 1-alkoxy-3-phenylseleno-1-alkenes or 3-phenylselenoalkanal.
- 6) When the reaction of α,β -unsaturated aldehyde with **1** was carried out, side reactions took place to afford complex mixtures.
- 7) Although Yamamoto et al. reported that the alkylation of chiral α,β -unsaturated acetals with Me₃Al (or *i*-Pr₃Al) proceeded smoothly to yield 1,4-adduct preferentially, the reason of high regioselectivity was not disclosed on this manuscript, see: J. Fujiwara, Y. Fukutani, M. Hasegawa, K. Maruoka, H. Yamamoto, *J. Am. Chem. Soc.* **1984**, 106, 5004.

3-phenylseleno-1-alkenes unaffected by the steric hindrance by the β alkyl group (entries 3 and 8).

When 1-ethoxy-3-phenylseleno-1-propene was treated with aq. HCl, the hydrolysis of the vinyl ether function proceeded to afford 3-phenylseleno-pentanal in quantitative yield. We next examined the one pot synthesis of 3-phenylselenoalkanal (**4**) based on the reaction of α,β -unsaturated acetals with **1** and subsequent hydrolysis with aq. HCl. The results of the synthesis of various 3-phenylselenoalkanal by using this one pot method are also shown in Table 1.⁷⁾