Efficient Transformations of Trithio- and Triseleno-orthoesters into Ketene Dithio- and Diseleno-acetals

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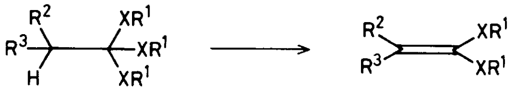
Sequential treatment of trithio- and triseleno-orthoesters with a Lewis acid followed by a base leads to ketene dithio- and diseleno-acetals in good yield; $SnCl_4$ or $TiCl_4$ and $Pr^i{}_2EtN$ or Et_3N are the most efficient reagents.

Ketene dithioacetals are valuable multi-purpose intermediates in organic synthesis[1] and their selenium analogues also display promising properties.[2] Although the preparation of the former compounds is well documented,[3] it often requires sophisticated starting materials or delicate reagents. Ketene diselenoacetals are of more limited access.[4] Our continuing studies of selenium-stabilized carbenium ions or equivalents thereof led us to investigate the reaction of triseleno-orthoesters with Lewis acids. We report here our preliminary results on a fast and simple method for transforming trithio- and triseleno-orthoesters into the corresponding ketene dithio- and diseleneo-acetals.

We found that sequential treatment of triseleno-orthoesters in methylene chloride solution with tin tetrachloride and a base such as di-isopropylethylamine (Hünig's base) produced ketene diselenoacetals in good to excellent yield. The reaction is easily extended to the corresponding thio derivatives (Scheme 1). Representative results in both the thio- and seleno-series are shown in Table 1.†

We found that tertiary amine bases are best suited for these transformations. No ketene acetal was observed in the presence of solid calcium carbonate and complete decomposition of the seleno-orthoesters to unidentified products occurred in the absence of any base. Pyridine and di-isopropylamine gave less satisfactory (21 and 68% respectively) yields of (**2b**). On the other hand, (**2b**) was isolated in



(**1**) X = S
(**3**) X = Se

(**2**) 10—89%
(**4**) 59—86%

Scheme 1. *Reagents:* $SnCl_4$, CH_2Cl_2, −40 °C, then $Pr^i{}_2EtN$, −40 °C to room temp.

Table 1. Preparation of ketene dithio- and diseleno-acetals[a] according to Scheme 1.

X	R^1	R^2	R^3	Product	Yield[b] (%)
S	Me	Me	Me	(**2a**)	10
	Me	Pr^n	H	(**2b**)	89
	Ph	H	H	(**2c**)	64
	Ph	Me	H	(**2d**)	72
Se	Me	H	H	(**4a**)	65
	Me	Pr^n	H	(**4b**)	86
	Ph	H	H	(**4c**)	59
	Ph	Me	H	(**4d**)	67

[a] All new compounds exhibited i.r., ^1H n.m.r., and mass spectra in agreement with the structures proposed. [b] Isolated yields after t.l.c.

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† In a typical experiment triphenyl triseleno-orthopropionate (1 mmol) was dissolved in dry CH_2Cl_2 (4 ml) and cooled to −40 °C under argon. $SnCl_4$ (1.2 mmol) dissolved in CH_2Cl_2 (1 ml) was added dropwise to the stirred solution, followed after 10 min by $Pr^i{}_2EtN$ (1.2 equiv.) in CH_2Cl_2 (1 ml). Stirring was continued for 10 min at −40 °C, then the temperature was allowed to reach room temperature during 20 min. After filtration on Celite the solvent was evaporated off and the crude product purified by t.l.c. (SiO_2, Et_2O–pentane, 1:99). 1,1-bis(phenylseleno)propene (**4d**) was isolated as a pale yellow oil in 67% yield.

nearly quantitative yield when triethylamine was used in the place of Hünig's base.

The nature of the Lewis acid is also of prime importance for the success of the reaction. Thus, (**2b**) is obtained in 80% yield using $TiCl_4$, $ZnCl_2$ gives only 12% of product after 22 h at room temperature, and the reaction does not proceed at all with $AlCl_3$.

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