Preparation of Dithio-, Thioseleno-, Thiosilyl-, and Thiostannyl-keten Acetals

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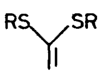
Summary α-Lithiovinylphenyl sulphide reacts with a series of electrophiles to give dithio-, thioseleno-, thiosilyl-, and thiostannyl-keten acetals.

KETEN thioacetals (**1**) and the derived monosulphoxides (**2**) are useful reagents in organic synthesis.[1] The methods used to prepare keten thioacetals are not applicable to a general representation of keten acetals (**3**). Here we report a simple, one-step method applicable to a variety of compounds of the type (**3**). Formation of the α-lithiovinyl phenyl sulphide anion (**4**) is usually accomplished using alkyl-lithium compounds to deprotonate vinyl phenyl sulphide.[2] We have found this procedure both inconvenient and inconsistent, since the products are invariably contaminated by addition of the alkyl-lithium to the vinyl phenyl sulphide [*i.e.* (**5**)]. The method recently reported by Cookson[3] [lithium di-isopropylamide in tetrahydrofuran (THF)–hexamethylphosphoric triamide (HMPA) (9:1)] is a marked improvement since no addition takes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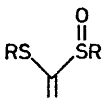
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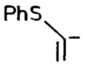
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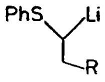
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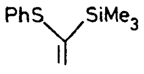
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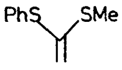
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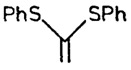
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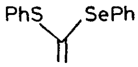
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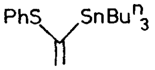
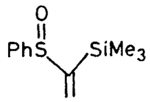

(10)

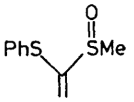
place, but HMPA is difficult to remove from our products. A convenient procedure is to add a solution of the required electrophile (Y) in THF to a slurry of lithium di-isopropylamide in hexane at −78 °C. In this way excellent yields of products (**3**) (Table) are obtained without any by-products with simple work-up. Oxidation of the keten acetals (**3**) using a method developed by Russell[4] (0·5M $NaIO_4$–H_2O–MeCN, −10 °C) gave slow (24—48 h) but clean conversions into the corresponding sulphoxides or selenoxide. However, oxidations with *m*-chloroperbenzoic acid (Table) were much more rapid (5—10 min) and convenient. The selective oxidation of (**3**; X = PhS, Y = MeS) is noteworthy.

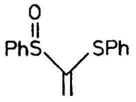
TABLE. Reactions of (**4**) with electrophiles (Y) and the oxidation of the products.

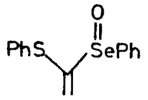
Electrophile	Product (yield/%)[a]	Oxidation product[b]
$ClSiMe_3$	(**6**) (97)	(**11**)
MeSSMe	(**7**) (61)	(**12**)
PhSSPh	(**8**) (59)	(**13**)
PhSeBr	(**9**) (84)	(**14**)
$ClSnBu^n_3$	(**10**) (87)	(**15**)

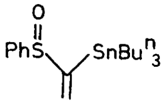
[a] The yields refer to pure distilled products. [b] Oxidations were carried out using *m*-chloroperbenzoic acid (1 equiv.) in dichloromethane at −78 °C. All the sulphoxides and the selenoxide were formed in 90—100% yield of pure isolated compounds.


(**11**)


(**12**)


(**13**)


(**14**)


(**15**)

All new compounds gave spectral and analytical data in agreement with assigned structures.

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