Unexpectedly Easy Formation of α-Seleno-Carbonyl Compounds from Vinyl Selenides

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Summary Seleno-carbonyl compounds are formed on reaction of seleninic acid or anhydride with vinyl selenides and vinyl sulphides.

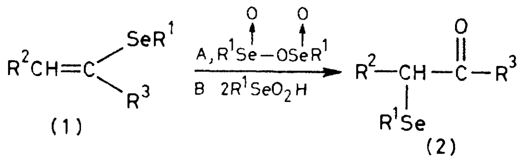
α-SELENO-ALDEHYDES and -KETONES are valuable building blocks in organic synthesis They are regiospecifically alkylated[1] and hydroxyalkylated[2] and can be transformed into a variety of selenium-free derivatives[3] including α-enones [1,2,4] They have already been prepared from carbonyl compounds,[1] olefins,[5] enol ethers,[6] α-halogeno-selenides,[7] β-hydroxyselenides,[6,8,9] and α-selenoalkyl lithium compounds [4]

TABLE 1

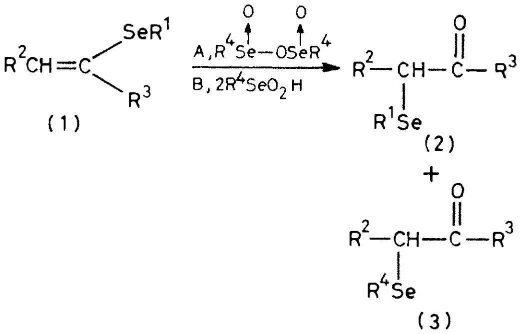
Compounds (**1**)	Yield of compounds (**2**)[a]/% (method, T/°C, t/h)
a	82 (A, 20, 40)
	83 (B, 20, 15 then 50, 2)
b	52 (A, 20, 24)
	41 (B, 50, 7)
c	84 (A, 20, 23)
	84 (B, 20, 77)
d	44 (A, 20, 9)
	36 (B, 50, 6)

[a] Compounds (**2**) were purified by preparative thick layer chromatography, all are liquids

We report here that they can also be conveniently prepared from vinyl selenides on reaction with seleninic anhydride (1 equiv, $CHCl_3$, 20—50 °C, method A), a valuable reagent recently developed by Barton *et al*,[10] or on reaction with seleninic acid (2 equiv, $CHCl_3$, 20–50 °C, method B) [equation (1) and Table 1] † In all the cases studied, the α-seleno-carbonyl compound is formed along with the diselenide and seleninic acid from which it can be easily freed To establish the reaction mechanism we used a vinyl selenide and a seleninic anhydride or acid each bearing a different group on the selenium atom We found [equation (2), Table 2] that phenylseleninic anhydride or acid exclusively produces the α-phenylseleno-carbonyl compound whatever phenyl or methyl vinyl selenide is used However, a 1 : 1 mixture of both methylseleno- and phenylseleno-carbonyl compounds is obtained on the reaction of methylseleninic anhydride or acid with phenyl vinyl selenides These results imply, at least for the latter case, the intervention of the selenyl-group arising from the vinyl selenide



$$R^2CH{=}C(SeR^1)R^3 \xrightarrow[\text{B } 2R^1SeO_2H]{\text{A}, R^1\overset{O}{\overset{\uparrow}{Se}}-O\overset{O}{\overset{\uparrow}{Se}}R^1} R^2-\underset{R^1Se}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-R^3 \quad (1)$$



$$R^2CH{=}C(SeR^1)R^3 \xrightarrow[\text{B}, 2R^4SeO_2H]{\text{A}, R^4\overset{O}{\overset{\uparrow}{Se}}-O\overset{O}{\overset{\uparrow}{Se}}R^4} R^2-\underset{R^1Se}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-R^3 + R^2-\underset{R^4Se}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-R^3 \quad (2)$$

a, $R^1 = Ph$, $R^2 = C_9H_{19}$, $R^3 = H$, $R^4 = Me$
b, $R^1 = Ph$, $R^2 = C_8H_{17}$, $R^3 = Me$, $R^4 = Me$
c, $R^1 = Me$, $R^2 = C_9H_{19}$, $R^3 = H$, $R^4 = Ph$
d, $R^1 = Me$, $R^2 = C_8H_{17}$, $R^3 = Me$, $R^4 = Ph$

[R^4 applies only to compounds (**3**)]

TABLE 2

Compounds (**1**)	Method (T/°C, t/h)	Yield of (**2**) %	Yield of (**3**) %
a	A (20, 15 then 50, 6)	35	39
	B (20, 15 then 50, 14)	40	44
b	A (50, 7)	16[a]	—
c	A (20, 5)	—	79
	A (50, 1)	—	81
	B (20, 7)	—	78
d	A (20, 9)	—	58
	B (20, 9)	—	50

[a] Several other products are formed in this reaction

Furthermore, both methods A and B allow the formation of (2-phenylseleno)heptanal and phenylselenoethanal, respectively, from (1-phenylthio)hept-1-ene [61% (method A) and 68% (method B)] and from ethyl vinyl ether [30% (method A), not optimized] However, under similar conditions, 1-morpholinocyclopentene leads only to a tarry material

The precise mechanistic details of this transformation are not known at present

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† All compounds gave satisfactory combustion and spectroscopic analyses

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