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A NEW SYNTHESIS OF PHENYLVINYLSELENIDES

Derek H.R. Barton*, George Bashiardes and Jean-Louis Fourrey

Institut de Chimie des Substances Naturelles, C.N.R.S.,
91190 Gif-sur-Yvette, France

Abstract. Ketonic hydrazones react smoothly at room temperature in tetrahydrofuran in presence of an excess of t-butyltetramethylguanidine with phenylselenenyl bromide to give good to excellent yields of phenylvinylselenides.

Phenylvinylselenides are of considerable synthetic interest.[1] We herein report a new and convenient method for their preparation starting from ketones.

We had previously shown[2] that the synthesis of vinyl iodides by oxidation of hydrazones with iodine[3] could be significantly improved by using strong, hindered guanidines[4] as bases. The theory of the iodine oxidation of hydrazones[2,3] suggested that a similar reactivity should be observable with other electrophiles, for example phenylselenenyl bromide (Scheme). As with the iodine oxidation an application to hindered carbonyls could be envisaged.

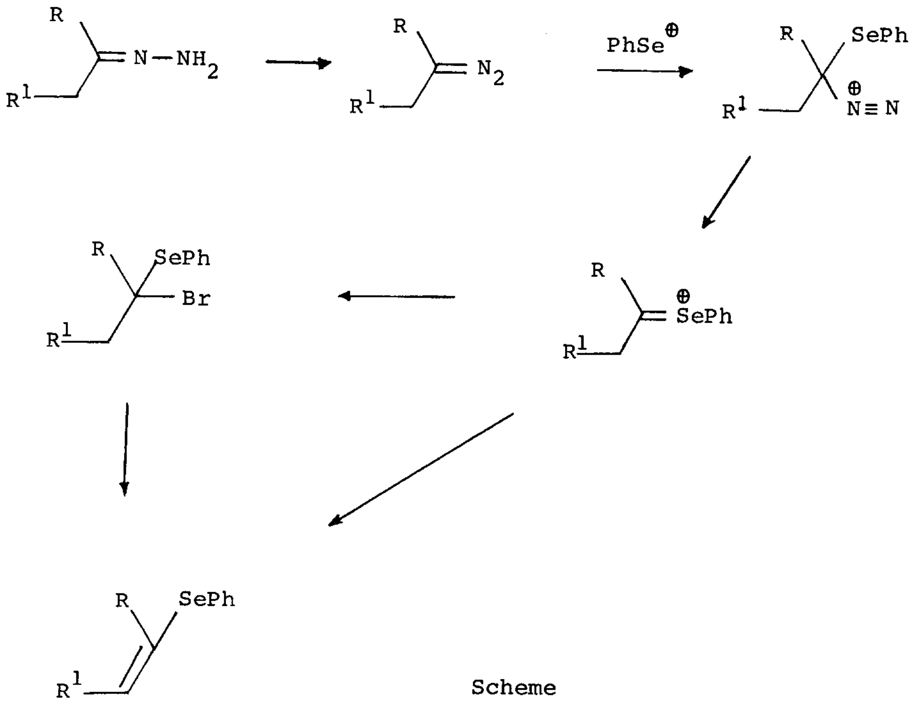
In the event the addition of a hydrazone in dry tetrahydrofuran in the presence of 5 equivalents of t-butyltetramethylguanidine to an excess (10-12 equivs) of freshly prepared phenylselenenyl bromide in the same solvent gave good to excellent yields of phenylvinylselenides. The results are given in the Table.

A typical experimental procedure is as follows. Bromine (0.1 ml, 2 mmol) in dry (sodium) tetrahydrofuran (5 ml) was added slowly with stirring to diphenyldiselenide (0.85 g, 2.7 mmol) in the same solvent (20 ml). After 30 mins. 3β-hydroxypregn-5-en-20-one hydrazone[3] (150 mg, 0.45 mmol) in tetrahydrofuran (10 ml) containing t-butyltetramethylguanidine (20 mmol) was added dropwise.

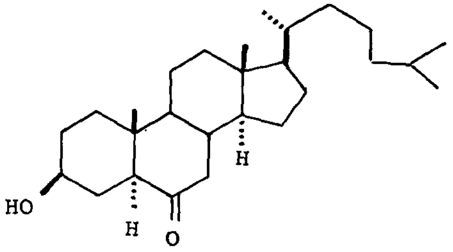
The solvent was removed in vacuo and the residue in ether was washed with 2N aqueous hydrochloric acid, water and aqueous sodium sulphite. The product was chromatographed over silica (hexane-ethyl acetate : 80-20) to give diphenyldiselenide and compound (7).

The formation of (7), a single isomer with the configuration probably as indicated, was unexpected, since 20-hydrazone oxidation with iodine gives only vinyl (20, 21-) iodide.[2] The structure was confirmed by reduction with sodium and ethanol to a mixture of stereoisomeric olefins, one component of which was synthesised by a Wittig reaction.[5]

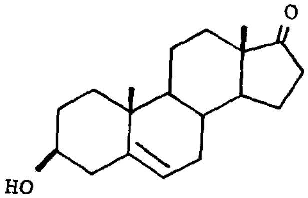
The reaction of diazomethane with phenylselenenyl bromide to give $PhSeCH_2Br$ has already been reported in the literature.[6]



Scheme



(1)



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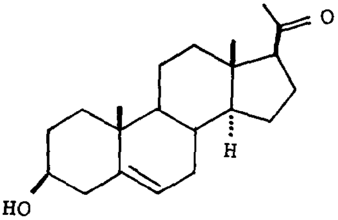

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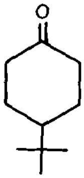

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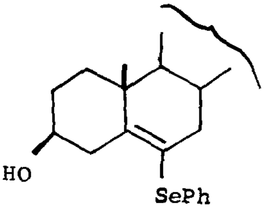

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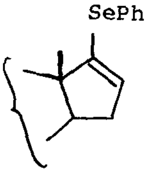

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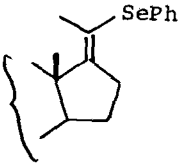
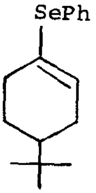


(7)



(8)

Table

Starting Ketone	Vinyl Selenide : Yield %		M.p. °C	λmax. mμ : (ϵ) in EtOH	$[\alpha]_D$: 1% in $CHCl_3$
(1)	(5)	87	126-128	259 (8070)	-26°
(2)	(6)	90	171-173	257 (6340)	-86°
(3)	(7)	83	148-150	260 (8440)	-60°
(4)	(8)	70	-	255 (9250)	-

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