Cyanamidoselenenylation of Alkenes

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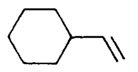
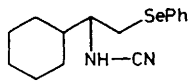
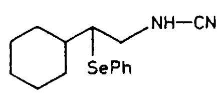
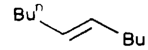
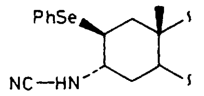
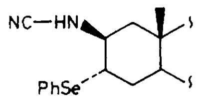
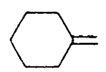
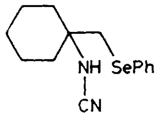
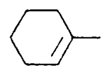
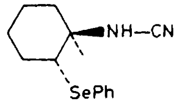
The acid catalysed reaction of alkenes with *N*-phenylselenophthalimide and cyanamide affords β-phenylseleno cyanamides, which can be easily transformed into cyanamides, allylic cyanamides, or cyanimides.

In view of the versatile chemistry of organoselenium compounds the introduction into alkenes of both phenylseleno and nitrogen functional groups (aminoselenenylation of alkenes) should provide a valuable tool for synthetic strategies.[1,2] In a previous communication[2] we reported that the reaction of phenylselenenyl chloride with alkenes and several carbamates, in the presence of silver tetrafluoroborate, affords β-phenylseleno carbamates in good yields.

We report now that cyanamide adds smoothly to alkenes in the presence of *N*-phenylselenophthalimide (N-PSP) as selenenylating agent and toluene-*p*-sulphonic acid (*p*-TsOH) as catalyst to produce β-phenylseleno cyanamides. The results

Table 1. Cyanamidoselenenylation of alkenes.[a]

Entry	Alkene	Temp. /°C; time/h	Product (s)[b]	% Yield[c]
1		25; 22	 (1)  (2)	50[d]
2		25; 24	(1) (2)	81[d,e]
3		25; 22	*erythro*-(3)	78
4		25; 5	*erythro*-(3)	62[f]
5		25; 22	*threo*-(3)	81
6	5α-Cholest-2-ene	25; 18	 (4)  (5)	92[g]
7		25; 3	(4) (5)	41[f,g]
8		25; 24	 (6)	71
9		25; 24	 (7)	78

[a] General procedure: to a solution of the alkene (1 mmol), H_2NCN (20 mmol), and *p*-TsOH (1 mmol) in dry CH_2Cl_2 (30 ml), was added dropwise, in the dark and under argon, at 25 °C a solution of N-PSP (1.3 mmol) in dry CH_2Cl_2 (3 ml) over 1 h. The reaction mixture was then stirred at 25 °C for the stated times and after usual work-up purified by column chromatography on silica gel. [b] All products have been fully characterized by spectral analysis. [c] Regioisomers, when present, were separated chromatographically. [d] Ratio (1):(2) 1:1. [e] Only 0.5 mmol of *p*-TsOH was employed. [f] PhSeCl (1.2 mmol) and $AgBF_4$ (1.3 mmol) were used instead of N-PSP-*p*-TsOH. [g] Ratio (4):(5) 3:2.

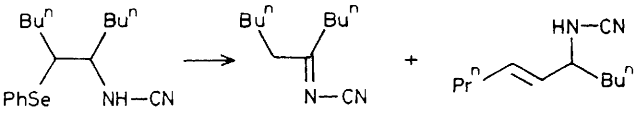
obtained with different substrates are shown in Table 1. This cyanamidoselenenylation proceeds well with mono-, di-, and tri-substituted alkenes.

It is noteworthy that clean reactions and pure products were isolated in good yields despite the long reaction times needed.

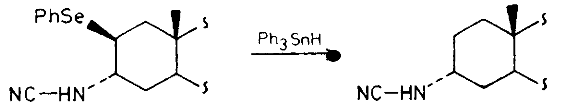
Table 2. Oxidative elimination of the phenylseleno group of *erythro*-(3).

Oxidant	Solvent	Temp./°C; time/h	Products(s) (% Yield)
O_3	CCl_4	80; 2	(8) (61); (9) (30)[a]
H_2O_2[b]	THF[d]	0; 48	(9) (59)[c]
H_2O_2[b]	MeOH	0; 72	(8) (10); (9) (71)
H_2O_2[b]	Et_2O	0; 48	(9) (77)[c]

[a] Ozonization was carried out in CH_2Cl_2 at −78 °C, followed by addition to refluxing CCl_4. [b] 2 mmol of 15% H_2O_2 per mmol of substrate. [c] Cyanimide (8) was not isolated. [d] THF = tetrahydrofuran.


erythro-(3) (8) (9)

Scheme 1


(4) (10)

Scheme 2

However, when the reagents PhSeCl–$AgBF_4$ were used instead of N-PSP-*p*-TsOH, a system which has proved to be efficient for the carbamatoselenenylation of alkenes,[2] the reaction times were shorter although the yields were lower (compare entries 3,4 and 6,7).†

With mono- and 1,2-disubstituted alkenes *ca.* 1 : 1 mixtures of regioisomers were obtained. Nevertheless, high regioselectivity is observed with 1,1-disubstituted and trisubstituted alkenes, the Markownikov adducts being exclusively formed (entries 8 and 9).

The stereochemical course of the reaction was investigated using *Z*- and *E*-dec-5-ene as substrates. A different diastereoisomer of 5-cyanamido-6-(phenylseleno)decane (3) was obtained selectively from *Z*- or *E*-dec-5-ene (Table 1, entries 3—5). These stereoisomers were clearly distinguished by their ^1H and ^{13}C n.m.r. spectra.

Oxidative elimination of the phenylseleno group led to a mixture of allylic cyanamides and cyanimides (the latter produced by isomerization of the initially formed vinylic cyanamides). The regioselectivity of the deselenenylation reaction could be improved by an appropriate choice of the reaction conditions as shown in Table 2 for *erythro*-(3) (Scheme 1).

This reaction is equivalent to a nucleophilic addition to a double bond as was explicitly demonstrated for compound (4)

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† The system N-PSP–HBF_4 can be advantageously used to accomplish the carbamatoselenenylation of alkenes instead of the previously reported PhSeCl–$AgBF_4$.[2] This overcomes the difficulty of working with the very hygroscopic and expensive $AgBF_4$, and also provides an easier work-up procedure.

which, upon reaction with Ph_3SnH (3 mmol/mmol substrate, toluene, 120 °C, 2 h),[3] gave (**10**) in 94% yield (Scheme 2).

This cyanamidoselenenylation reaction together with our recently reported[4] thermal allylic transposition of allylic cyanamides allows a great variety of allylic cyanamides, as well as cyanamides and cyanimides, to be synthesised readily. We also consider that this reaction complements the known halogenocyanamination of alkenes[5] and compares advantageously if allylic cyanamides are required.

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