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NEW SYNTHESIS OF UNSTABILIZED SELENENAMIDES

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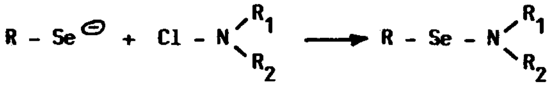
Abstract : Reaction of selenolates anions with N-chloroamines affords selenenamides in moderate to good yields.



During our investigations for a better understanding of rubber vulcanization mechanisms by organoselenium probes, we synthesized several selenenamides, substances recognized for a long time as vulcanization accelerators. The chemistry of selenenamides, the first synthesis of which appeared in 1975(1) has been recently reviewed(2). These amides, as well as their imidic analogs, have been used mainly as a source of R Se$^+$, cationic species in organic functional transformations(3). They have also been used as intermediates for synthesizing heterocycles(4). Selenenamides are relatively unstable but they can be stabilized in aromatic series by the introduction of an electron withdrawing group in the ortho position (i.e. C = O or - NO$_2$)(5) to the Se-N moiety.

Most of the synthetic pathways involve a reaction between a selenyl halide and an amine. We found that the formation of seleneny1 halides derived from diselenides bearing other selenium atoms is very difficult. It is also well known that the oxidation of thiols in the presence of an amine allows the formation of sulfenamides(6). In our hands, this method applied to selenols always led to the formation of the correspondint diselenide. We looked therefore for a new method of synthesis involving reversed polarization, i.e. a selenol reacting with an haloamine. A reaction of this type has been described between N-chlorosuccinimide and diphenyldiselenide affording N-phenylseleno-succinimide(7). N-haloamines have been known for a long time, and although rather unstable, are easily generated in solution from amines and sodium hypochlorite. We have shown that the selenolate species, obtained by reduction of a diselenide with NaBH$_4$, reacts with an ether solution of various N-chloroamines and gives the corresponding unstabilized selenenamides with moderate to good yields. Our method is quite general, as exemplified in Table 1.

Table 1

Selenenamides (a)	Yields (%)(b)	Mp °C	^{77}Se shifts (d)
(c) N-(BT-Se)-morpholine *	82	92-99	955.7
BT-Se-N(t-butyl)$_2$ *	49	104-107	710.3
N-(BT-Se)-phtalimide *	71	160-164	530.8
N-BT-Se)-pyrrole *	24	168-172	367.1
BT-Se-N-(allyl)$_2$ *	69	155-164	530.9
N-(PhCH$_2$-Se)-morpholine *	23	126-131	611.1
N-(Ph-Se)-succinimide	49	102-107 (7)	1181.4
N-(Ph-Se)-phtalimide	56	170-172 litt.171-175(7)	1139.9

(a) BT = 2-benzothiazolyl (b) yields are given for pure isolated products

(c) all the new compounds (*) were characterized by IR, ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy (CDCl$_3$, 400 MHz for ^{1}H) and by mass spectrometry. We did not find any relationship between the pK$_a$ values of the amines and the ^{77}Se chemical shifts of the selenenamides.

(d) for known selenamides, ^{77}Se chemical shifts range generally from 600 ppm to 1000 ppm(5,8)

Typical procedure

A solution of 25 mmoles of sodium hypochlorite in 240 ml of water and 200 ml of ether are added simultaneously to a cold (0°C) solution of 22 mmoles of the amide hydrochloride in 80 ml of water. Stirring is continued for 1 h and the organic phase is collected and dried (solution 1).

A solution of 12 mmoles of diselenide in 100 ml of ethanol is refluxed with 15 mmoles (0.57 g) of sodium borohydride. After 30 min, the solvent is removed by evaporation and solution 1 is added. After stirring 2 h at room temperature, the organic phase is washed with water, dried, evaporated and the selenenamide is recrystallized from toluene.

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