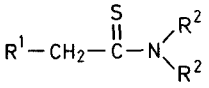
A Convenient Method for the Preparation of Substituted Selenoamides and Thioamides

Ramesh S. SUKHAI, Rob de JONG, Lambertus BRANDSMA*

Department of Organic Chemistry of the University, Croesestraat 79, Utrecht, The Netherlands

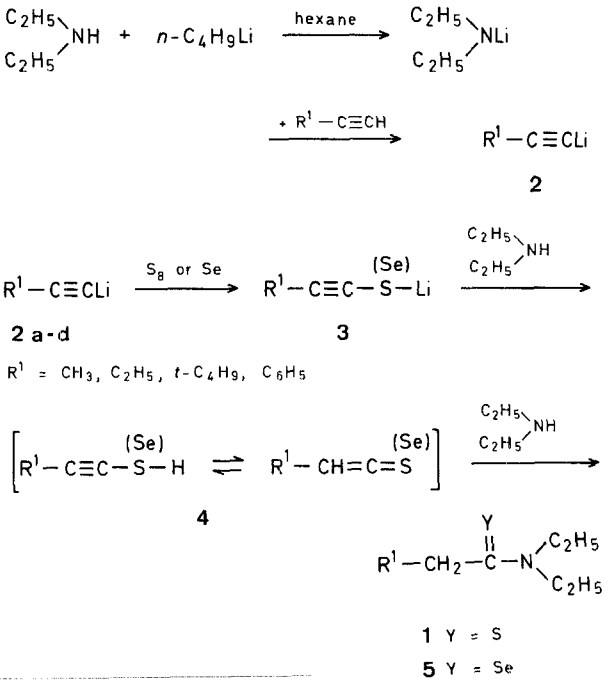
Thioamides **1** have been prepared in good yields by adding sulfer powder to a solution of lithium acetylenides R—C≡C—Li in an excess of diethylamine. In a similar fashion, the corresponding selenoamides were obtained in high yields.



1

Thioamides **1** have been prepared by adding alkynethiolates to a mixture of a secondary amine and *t*-butyl bromide[1], or by reacting thiadiazoles dissolved in amines with pellets of potassium hydroxide[2]. Selenoamides **5** have also been obtained in the same way, starting from the selenadiazoles[2], by adding hydrogen selenide to a nitrile[3], or by reaction of amides with phosphorus pentaselenide[4].

In this communication we wish to report a simple, high yield method, which is even shorter than the methods known in the literature.



2 a-d

R^1 = CH_3, C_2H_5, t-C_4H_9, C_6H_5

3

4

1 Y = S

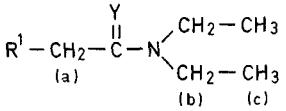
5 Y = Se

Table 1. Preparation of Thioamides **1** and Selenoamides **5**

Product	R^1	Y	Yield [%]	m.p. or b.p./torr	n_D^{20}	Molecular formula[a]
1a	CH_3	S	79	105°/16	1.5295	$C_7H_{15}NS$ (145.3)
1b	C_2H_5	S	97	72°/0.05	1.5240	$C_8H_{17}NS$ (159.3)
1c	t-C_4H_9	S	99	111°/1.5	1.5142	$C_{10}H_{21}NS$ (187.3)
1d	C_6H_5	S	85	57–58°	—	$C_{12}H_{17}NS$ (207.3)
5a	CH_3	Se	75	121°/16	1.5728	$C_7H_{15}NSe$ (192.2)
5b	C_2H_5	Se	97	90°/0.04	1.5600	$C_8H_{17}NSe$ (206.2)
5c	t-C_4H_9	Se	98	109°/0.01	1.5470	$C_{10}H_{21}NSe$ (234.2)
5d	C_6H_5	Se	83	71–72°	—	$C_{12}H_{17}NSe$ (254.2)

[a] All products (except **1d** and **5a**) gave satisfactory microanalyses (C ±0.4%, H ±0.13%).

Table 2. ^{1}H-N.M.R. and Mass Spectral Data for Thioamides **1** and Selenoamides **5**



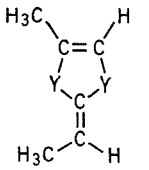
Product	^{1}H-N.M.R. (CCl_4): δ [ppm][a] H(a)	H(b)	H(c)	R^1	M.S. m/e (M^+)[b]
1a	2.52 (q, 2H)	3.41 (q, 2H), 3.76 (q, 2H)	1.16 (m, 9H)		145
1b	2.48 (m, 2H)	3.40 (q, 2H), 3.85 (q, 2H)	1.16 (t, 3H), 1.23 (t, 3H)	0.93 (t, 3H)	159
1c	2.60 (s, 2H)	3.45 (q, 2H), 3.82 (q, 2H)	1.16 (t, 3H), 1.22 (t, 3H)	1.00 (s, 9H)	187
1d	4.16 (s, 2H)	3.40 (q, 2H), 3.90 (q, 2H)	1.03 (t, 3H), 1.23 (t, 3H)	7.2 (s, 5H)	207
5a	2.70 (q, 2H)	3.43 (q, 2H), 3.90 (q, 2H)	1.26 (m, 9H)		193
5b	2.63 (m, 2H)	3.40 (q, 2H), 3.86 (q, 2H)	1.06 (m, 9H)		207
5c	2.84 (s, 2H)	3.50 (q, 2H), 4.00 (q, 2H)	1.23 (t, 3H), 1.26 (t, 3H)	1.03 (s, 9H)	235
5d	4.33 (s, 2H)	3.40 (q, 2H), 4.00 (q, 2H)	1.00 (t, 3H), 1.26 (t, 3H)	7.22 (s, 5H)	255

[a] Varian EM-360, 25% % solution in CCl_4, $(CH_3)_4Si$ (δ = 0 ppm) as internal standard.

[b] For Selenoamides $M^{\oplus}$ for the ^{80}Se isotopic species is given.

The products **1** or **5** were almost pure after removal of the excess of diethylamine. Further purification was achieved by either distillation or by crystallisation from dichloromethane and pentane. The structure of the products was corroborated by I.R.-, N.M.R.-, and Mass spectroscopy (see Table 2).

In the case of $R^1 = CH_3$, the same procedure as described below was used, except that no hydrochloric acid was added. Instead ether was added and the solutions filtered off; the products **1** or **5** were isolated in the usual way. When dilute hydrochloric acid was added, we also obtained the dimeric products **6** or **7** of methylthioketene or methylselenoketene, respectively.



6 Y = S

7 Y = Se

General Procedure for Thioamides 1 and Selenoamides 5:
To an excess of diethylamine (52 ml) at −30° is added a hexane solution of *n*-butyllithium (0.05 mol) at such a rate that the temperature of −30° is maintained. A yellow suspension is formed. The acetylene (0.05 mol) in an equal volume of cold (−30°) ether is then added and the temperature is allowed to rise. The mixture is then heated under reflux and sulfur or selenium powder (0.05 mol) is added. Refluxing is continued for 1 h and dilute hydrochloric acid (100 ml) is added (except for $R^1 = CH_3$ when ether is added). The brown upper layer is separated, the aqueous layer is extracted with ether and the combined ether solution is dried with magnesium sulfate. The ether is removed in vacuo and the residue is distilled under reduced pressure (recrystallised for $R^1 = C_6H_5$) to give the pure product. For yields and physical properties see Table 1.

Received: August 12, 1977

[1] P. J. W. Schuijl, L. Brandsma, *Recl. Trav. Chim. Pays-Bas* **87**, 38 (1968).
[2] F. Malek-Yazdi, M. Yalpani, *Synthesis* **1977**, 328.
[3] C. Collard-Charon, *Bull. Soc. Chim. Belges* **72**, 304 (1963).
[4] K. A. Jensen, P. H. Nielson, *Acta Chem. Scand.* **20**, 597 (1966).