# Chemoselective Reduction of Organoselenocyanates to Diselenides

Alain Krief,* Cathy Delmotte and Willy Dumont

Department of Chemistry, Facultés Universitaires Notre-Dame de la Paix, 61 rue de Bruxelles B-5000, NAMUR (Belgium)

Abstract : Selenocyanates possess an extremely high propensity to produce diselenides on reaction with selenols or selenolates. This is effectively observed when one molar equivalent of metal hydride or lithium triethyl borohydride or one fourth molar equivalent of metal borohydrides are reacted with organic selenocyanates. © 1997 Published by Elsevier Science Ltd.

Organoselenocyanates play an important role in organoselenium chemistry. They are readily available and stable compounds which are easily transformed to valuable basic organoselenium reagents or compounds[1] especially to selenols and selenolates. The first transformation has been for long carried out with hypophosphorous acid[2a-c] and the second one with sodium borohydride[2d-e] (Scheme 1, left). More recently Salama described[3] that lithium triethyl borohydride and diisobutyl aluminum hydride produce either selenols or selenolates depending upon the amount (1 or 2 equivalents) of reducing agent used (Scheme 1, right).

Scheme 1
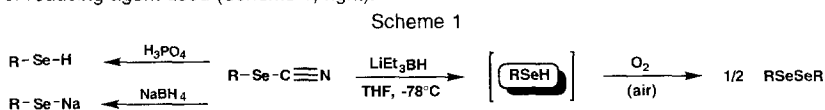
We now report that selenocyanates possess an extremely high propensity to produce diselenides on reaction with selenols or selenolates.[1a,b] This is effectively the case when one molar equivalent of metal hydrides or lithium triethyl borohydride (contrary to Salama's report)[3] or one fourth molar equivalent of metal borohydrides are used (Scheme 2).[4]
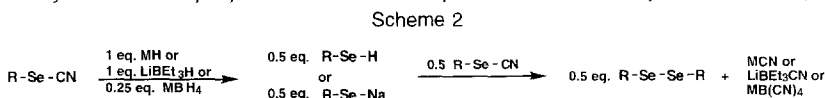
Scheme 2

Thus diselenides are produced from organoselenocyanates and one equivalent of sodium hydride in DMF at 20°C (Conditions A, Scheme 2, Table 1). The reaction is faster with phenyl selenocyanate and organoselenocyanates bearing small side chains (Table 1, Conditions A, entries a,b) and requires a longer time (13-21 h) to go to completion with those derivatives bearing long- or branched side chains (Table 1, Conditions A, entries c and d,e). Similar results have been obtained if sodium hydride is replaced by lithium or potassium hydride[4b] or if the reactions are carried out in THF instead of DMF. As a general trend the reaction is very slow in THF and requires a higher temperature (75°C instead of 20°C) to proceed. The highest reactivity of LiH compared to the other hydrides in THF (Table 1, Conditions B, compare entries b,f,g) probably accounts for its better solubility in this solvent.
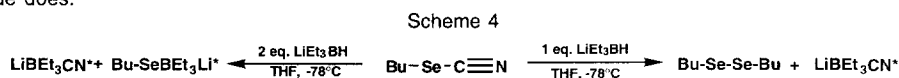
Table 1

Entry	R	MH	Conditions A	Yield in RSeSeR	MH	Conditions B	Yield in RSeSeR
a	Ph	NaH	DMF, 20°C, 2h	77	LiH	THF, 75°C, 4h	80
b	1-Bu	NaH	DMF, 20°C, 3.5h	90	LiH	THF, 75°C, 4h	96
c	1-Dec	NaH	DMF, 20°C, 2h, (13h)	30, (70)			
d	2-Pr	NaH	DMF, 20°C, 3h	55*	LiH	THF, 75°C, 20h	60
e	2-Dodec	NaH	DMF, 20°C, 16h	90			
f	1-Bu				NaH	THF, 75°C, 144h	93
g	1-Bu				KH	THF, 75°C, 108h	66

This reaction has been successfully extended to functionalized derivatives such as 5-chloro- and 5-bromo-pentyl selenocyanates. These provide di(5-chloropentyl)diselenide and di(5-cyanopentyl)diselenide respectively, free from the tetrahydroselenopyran which would have resulted from intramolecular cyclisation of the putative selenolate intermediate (Scheme 3). The case of 5-bromopentyl selenocyanate is particularly interesting (Scheme 3, entry b). Not only cyclisation does not take place, even in the presence of such a good leaving group, but also the substitution of the bromide by the cyano group occurs during the process.

Scheme 3

a	X=Cl	Y= Cl 52%
b	X= Br	Y= CN 67%
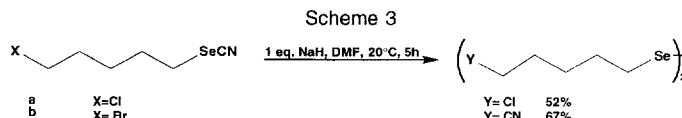
We have performed, under an argon atmosphere and according to the published procedure,[3] the reaction between n-butyl selenocyanate and one molar equivalent of lithium triethyl borohydride in THF. We found that dibutyl diselenide is directly produced (-78°C, 0.5h, 95%, Scheme 4). Therefore "the air oxidation" step described by Salama is not needed (Scheme 1, right) for the transformation he described.[3] We have also monitored the reduction of n-butyl selenocyanate by one molar equivalent of lithium triethyl borohydride, in an oxygen free atmosphere, by ^{77}Se NMR (THF, -78°C) and have confirmed our results : the peak attributed to the butyl selenocyanate (+216 ppm) is no longer present after a few minutes and is replaced by the one of dibutyl diselenide (+292 ppm).[5] The butylselenol or lithium selenolate were never detected[5] and if formed react faster with the unreacted n-butyl selenocyanate than lithium triethyl borohydride does.[4]

Scheme 4

$$\text{LiBEt}_3\text{CN}^* + \text{Bu-SeBEt}_3\text{Li}^* \xleftarrow[\text{THF, -78°C}]{\text{2 eq. LiEt}_3\text{BH}} \text{Bu-Se-C}\equiv\text{N} \xrightarrow[\text{THF, -78°C}]{\text{1 eq. LiEt}_3\text{BH}} \text{Bu-Se-Se-Bu} + \text{LiBEt}_3\text{CN}^*$$

* NMR experiments suggest that both lithium cyanide and lithium butyl selenolates are involved as complexed species.[5]

Finally, we have determined that dibutyl diselenide is produced chemoselectively when n-butyl selenocyanate is reacted, under argon, with 0.25 molar equivalent of sodium borohydride in ethanol or lithium borohydride in THF (Scheme 2, Table 2). The former reaction is faster (Table 2, compare entry a and b) and it was found that the first three hydrides are delivered much faster that the fourth. This will be reported in the full paper.

Table 2

Entry	MBH$_4$	Eq.	Conditions	BuSeSeBu	BuSeCN (recovered)
a	NaBH$_4$	0.25	EtOH, 20°C, 0.3h	73	-
b	LiBH$_4$	0.25	THF, 20°C, 1h	74	21

REFERENCES AND NOTES

1. (a) Rheinboldt, H. in 'Schwefel-, Selen-, Tellur- Verbindungen', Methoden der Organische Chemie (Houben Weyl) Müller, E. ed., Georg Thieme Verlag, Stuttgart, 1967, Vol 9. (b) Klayman, D.L. 'Organic Selenium Compounds: Their Chemistry and Biology', Klayman, D.L. and Günther, W.H.H. eds, John Wiley and Sons, Chichester, 1973, 67 (c) Paulmier, C. in 'Selenium Reagents and Intermediates in Organic Synthesis', Baldwin, J. E. ed., Pergamon Press, Oxford, 1986, Vol. 5 (d) Back, T.J. in 'The Chemistry of Organic Selenium and Tellurium Compounds' Patai, S.; Rappoport, Z. eds, John Wiley and Sons, Chichester, 1987, Vol. 2, Chap 3, pp 91 (e) Toshimitsu, A.; Uemura, S. in 'The Chemistry of Organic Selenium and Tellurium Compounds' Patai, S.; Rappoport, Z. eds, John Wiley and Sons, Chichester, 1987, Vol. 2, Chap 14, pp 541.
2. (a) Sekido, E.; Fernando, Q.; Freiser, H. Anal. Chem. 1964, 36, 1768 (b) Lakshmikantham, M. V.; Cava, M. P. J. Org. Chem. 1980, 45, 2632 (c) Lakshmikantham, M. V.; Cava, M. P. J.; Gorito, A. F. J.Chem. Soc. Chem. Commun. 1975, 383 (d) Sharpless, K. B.; Young, M. W. J. Org. Chem. 1975, 40, 947 (e) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. J. Org. Chem. 1978, 43, 1697.
3. Salama, P.; Bernard, C. Tetrahedron Lett., 1995, 32, 5711.
4. (a) Selenolates are obtained in good yields on reaction of organoselenocyanates with (i) 2 eq. NaH in DMF at 75°C (except from 2-dodecyl selenocyanate) (ii) 2 eq. LiBEt$_3$H in THF at 20°C[3] (iii) 1.25 eq. of NaBH$_4$ in ethanol (iv) 1.25 eq. LiBH$_4$ in THF (b) These results will be reported in the full paper.
5. MeSeMe as external standard. We also recorded, under similar conditions, the ^{77}Se NMR spectra of the following compounds or mixture of compounds : BuSeH (22 ppm); BuSeH-BEt$_3$ (-4 ppm); BuSeLi (-220 ppm); BuSeH-BEt$_3$-LiCN (-80 ppm).