A Convenient Procedure for the Reductive Deselenization of Selenides with Nickel Boride

Thomas G. Back

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

Nickel boride, readily produced *in situ* from nickel chloride hexahydrate and sodium borohydride, efficiently reduces selenides to hydrocarbons under mild conditions.

Synthetic transformations based upon organoselenium chemistry[1] frequently require the reductive removal of an arylseleno residue from the penultimate product. This has been most effectively accomplished in the past by free-radical deselenization with triphenyl-[2] or tri-n-butyl-tin hydrides.[3] Despite the versatility and widespread application of this method, disadvantages include the need for elevated temperatures, reaction times of several hours, and the relatively high cost and air-sensitivity of the tin hydride reagents. During the course of other work,[4] we recently observed that the ketene diselenoacetal (**1**) was more efficiently deselenized with nickel boride than with tin hydrides. To our knowledge, only one other isolated example of the use of this reagent in deselenization has been reported.[5] Since nickel boride is easily generated *in situ* from stable and inexpensive nickel chloride hexahydrate and sodium borohydride[6,7] a study of its general utility in reductive deselenization appeared warranted.

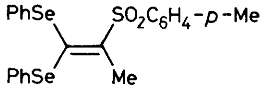
Preliminary results are listed in Table 1 and indicate that a variety of arylseleno compounds are readily cleaved with this reagent. Typically, sodium borohydride is added in small portions (vigorous reaction!) to a solution of the substrate and the nickel salt in tetrahydrofuran–methanol at 0 °C. Protection from the atmosphere is unnecessary. After an additional 10—15 min at 0 °C, the mixture is filtered through Celite and then purified by flash chromatography on silica gel. The entire operation can be performed in less than one hour.

Table 1 indicates the types of functionalities compatible with this method. It was of particular interest to determine whether deselenization could be achieved in the presence of alkenes and sulphides as nickel boride has been reported to hydrogenate carbon–carbon double bonds[7] and to desulphurize various organosulphur compounds.[6,8] Double bond

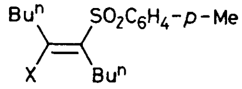
Table 1. Deselenizations with nickel boride.

Substrate	Molar ratio of substrate(s): $NiCl_2 \cdot 6H_2O$: $NaBH_4$	Product(s)[a]	Yield (%)[b]
(**2**)	1 : 4 : 12	(**3**)	95 (*E* : *Z* = 73 : 27)
(**4**)	1 : 2 : 6	(**5**)	80
(**6**)	1 : 2.3 : 6.9	(**8**)	90
(**6**),(**7**)	1 : 1 : 2 : 6	(**7**),(**8**)	97,102[c]
(**9**)	1 : 2.6 : 7.8	(**11**)	83
(**10**)	1 : 3,6 : 10.8	(**11**)	91
(**12**)	1 : 2.5 : 7.5	(**13**),(**14**)	60,34[d]
(**15**)	1 : 1.6 : 4.8	(**16**)	93
(**17**)	1 : 6 : 18	(**18**)	71
(**19**)	1 : 2 : 6	(**18**)	100
(**20**)	1 : 4 : 12	(**18**),(**21**)	29,50[d]

[a] All products were identified by their i.r., n.m.r., and mass spectra. New compounds (**7**), (**11**), and (**17**) gave satisfactory elemental analyses. [b] Isolated yields unless otherwise noted. [c] A theoretical yield of 100% of (**8**) is based on its quantitative formation exclusively from (**6**). [d] The unseparated mixture of products was isolated and their relative proportions determined by g.c. analysis.

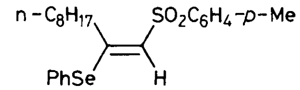


(1)



(2) X = PhSe

(3) X = H



(4)

n-$C_{10}H_{21}SO_2C_6H_4$-*p*-Me

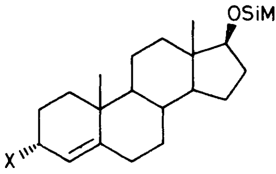
(5)

$X[CH_2]_{11}CO_2Me$

(6) X = PhSe

(7) X = PhS

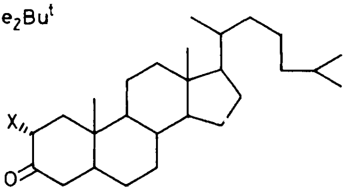
(8) X = H



(9) X = *o*-$NO_2C_6H_4Se$

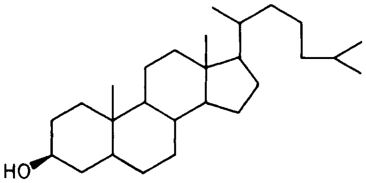
(10) X = *p*-$NO_2C_6H_4Se$

(11) X = H

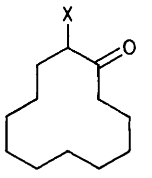


(12) X = PhSe

(13) X = H

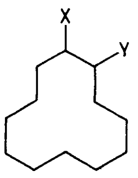


(14)



(15) X = PhSe

(16) X = H



(17) X = *p*-$NO_2C_6H_4Se$, Y = H

(18) X = Y = H

(19) X = PhSe, Y = Cl

(20) X = PhSe, Y = OAc

(21) X = H, Y = OAc

reduction was observed in only one case [(**4**) → (**5**)] and was not significant in the transformations (**2**) → (**3**), and (**9**) or (**10**) → (**11**). Furthermore, selenide (**6**) was reduced to (**8**) with high selectivity in the presence of the analogous sulphide (**7**), presumably because of the greater strength of the C–S linkage. The β-chloro selenide (**19**) afforded cyclododecane (**18**) as the exclusive product, while the β-acetoxy derivative (**20**) gave the expected cyclododecyl acetate (**21**) together with a small amount of (**18**). Partial over-reduction [to (**14**)] was observed in the conversion of the α-seleno ketone (**12**) into cholestan-3-one (**13**), but not in that of (**15**) into cyclododecanone (**16**).

These preliminary experiments indicate that nickel boride is a convenient and effective reagent for a variety of reductive deselenizations.

Financial assistance from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Received, 20th June 1984; Com. 864

References

1 D. Liotta, *Acc. Chem. Res.*, 1984, **17**, 28; H. J. Reich, *ibid.*, 1979, **12**, 22; H. J. Reich in 'Oxidation in Organic Chemistry. Part C,' ed. W. S. Trahanovsky, Academic Press, New York, 1978, Ch. 1; D. L. J. Clive, *Tetrahedron*, 1978, **34**, 1049.

2 D. L. J. Clive, G. J. Chittattu, V. Farina, W. A. Kiel, S. M. Menchen, C. G. Russell, A. Singh, C. K. Wong, and N. J. Curtis, *J. Am. Chem. Soc.*, 1980, **102**, 4438.

3 K. C. Nicolaou, *Tetrahedron*, 1981, **37**, 4097, and references cited therein.

4 T. G. Back, S. Collins, U. Gokhale, and K.-W. Law, *J. Org. Chem.*, 1983, **48**, 4776.

5 D. H. R. Barton, M. R. Britten-Kelly, and D. Ferreira, *J. Chem. Soc., Perkin Trans. 1*, 1978, 1090.

6 W. E. Truce and F. E. Roberts, *J. Org. Chem.*, 1963, **28**, 961; W. E. Truce and F. M. Perry, *ibid.*, 1965, **30**, 1316.

7 Nickel boride can also be prepared from nickel acetate: C. A. Brown and H. C. Brown, *J. Am. Chem. Soc.*, 1963, **85**, 1003; H. C. Brown and C. A. Brown, *ibid.*, p. 1005.

8 R. B. Boar, D. W. Hawkins, J. F. McGhie, and D. H. R. Barton, *J. Chem. Soc., Perkin Trans. 1*, 1973, 654; J. Schut, J. B. F. N. Engberts, and H. Wynberg, *Synth. Commun.*, 1972, **2**, 415, and references cited therein.