Novel Synthesis of Organic Diselenides

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Summary Reaction of hydrogen selenide, aldehydes, and amines, followed by reduction with sodium borohydride, gives high yields of diselenides.

MOST methods for the preparation of organic diselenides are based on the displacement of halides or tosylates by nucleophilic selenium species.[1a] However, there are no efficient methods to convert other common functional groups into diselenides. The reactions of carbonyl compounds with hydrogen selenide and its salts under a variety of alkaline and acidic conditions give low yields of diselenides and selenoaldehyde oligomers, respectively.[1b–d] We have now found that aromatic and aliphatic aldehydes are converted readily and in excellent yields into pure diselenides by using a two-step, one-pot reaction involving (a) the reaction of the aldehyde, an amine, and hydrogen selenide and (b) treatment of the reaction mixture with sodium borohydride.

When a slight excess of hydrogen selenide was passed into a solution of benzaldehyde in the presence of 1 mol. equiv. of piperidine or morpholine in absolute ethanol, the solution rapidly turned brown in an exothermic reaction. After 10 min this mixture was treated with sufficient sodium borohydride (*ca.* 0·25 mol. equiv.) to give a clear, orange-yellow solution. Water precipitated yellow crystalline benzyl diselenide in 84% yield. In the absence of amine the yield was $<40\%$; with 0·1 equiv. of piperidine 3 days were required for an 88% yield. *NN'*-Benzylidenepiperidine, an aminal, reacted in 10 min to give 80% of benzyl diselenide. These results indicate amine catalysis, probably through the intermediacy of an aminal. When the final $NaBH_4$ reduction was omitted, the purity of the diselenide and yields were drastically reduced.

TABLE

Reaction of aldehydes with sodium hydrogen selenide[a]

Reactant	Product	M.p. (t/°C)	Yield (%)
Benzaldehyde	Benzyl diselenide	92—93[2]	86
p-Diethylaminobenzaldehyde	Bis-(4-*NN*-diethylaminobenzyl) diselenide dihydrochloride	200—202 (decomp.)	67
1-Naphthaldehyde	Bis-(1-naphthylmethyl) diselenide	134—135·5	92
2-Naphthaldehyde	Bis-(2-naphthylmethyl) diselenide	110—111	91
9-Anthraldehyde	Bis-(9-anthrylmethyl) diselenide	193—195 (decomp.)	90
Dodecanal	Bis(dodecyl) diselenide	29·5—30·5[3]	73

[a] Products gave satisfactory elemental analyses and structures were confirmed by n.m.r. and i.r. spectroscopy.

A convenient variant of the procedure [equation (1)] uses ethanolic sodium hydrogen selenide[2] to avoid handling toxic H_2Se gas.[1e] (see Table).

$$\mathrm{RCHO} + \mathrm{NaHSe} + \mathrm{HNR_2{\cdot}HCl} \xrightarrow{\mathrm{EtOH}} \xrightarrow{\mathrm{NaBH_4}} \mathrm{RCH_2SeSeCH_2R} \qquad (1)$$

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[1] D. L. Klayman and W. H. H. Günther, eds., 'Organic Selenium Compounds: Their Chemistry and Biology,' Wiley-Interscience, New York, 1973: (a) p. 87; (b) p. 96; (c) p. 249; (d) p. 246; (e) p. 36.

[2] D. L. Klayman and T. S. Griffin, *J. Amer. Chem. Soc.*, 1973, **95**, 197.

[3] E. Rebane, *Arkiv. Kemi*, 1966, **25**, 363.