SHORT PAPER

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A modified method to prepare diselenides by the reaction of selenium with sodium borohydride[†]

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With a 8:1 molar ratio of selenium to borohydride, sodium diselenide can be prepared conveniently and safely in alkaline aqueous or ethanol solution, which can be used directly to synthesise symmetric diselenides in high yields.

Keywords: diselenides, sodium borohydride

Diselenides are useful reagents and intermediates in organic synthesis. Some have good biological activities as selenium-enzyme mimics,[1] some have catalytic activities.[2] Many methods have been developed to prepare diselenides with their own merits and disadvantages.[3–6] Displacement of halogen from an alkyl halide by an alkali diselenide constitutes a direct method. Sodium diselenide can be obtained by several methods.[3c] The facile and extensively used method of Klayman used the reaction of selenium with sodium borohydride in protonic solvents. This method could be utilised directly in typical nucleophilic displacement reactions.[7] However, it still suffered from some disadvantages: powered selenium was added twice, there was considerable gas evolution including hydrogen or highly toxic hydrogen selenide with loss of selenium.

During our experiments using Klayman's method, sodium hydroxide was added to the reactive mixture by chance. Then, an interesting phenomenon was found: there was no gas expulsion and the reaction proceeded mildly. We now report these reactions.

Results and discussion

An alkaline aqueous solution of sodium diselenide was prepared by a reaction of a 8:1 molar ratio of selenium to $NaBH_4$ in an aqueous solution of NaOH, the reaction proceeded mildly without foaming. The characteristic brownish red solution of Na_2Se_2 was obtained according to Eqn(1), which is totally different from the reaction in neutral aqueous solution, showed as Eqn(2).[7] The Na_2Se_2 in this alkaline solution could be used directly to prepare dibenzyl diselenide, $(C_6H_5CH_2Se)_2$, from benzyl chloride, in 87% yield (lit.[7] yield 77%) and 2,2′-diselenodibenzoic acid, from 2-aminobenzoic acid, in 90% yield.

$$8Se + NaBH_4 + 8NaOH \longrightarrow 4Na_2Se_2 + NaBO_2 + 6H_2O \quad (1)$$

$$2Se + 2NaBH_4 + 6H_2O \longrightarrow Na_2Se_2 + 2H_3BO_3 + 7H_2 \quad (2)$$

Compared with Klayman's method, ours had some advantages: (1) the amount of NaBH4 to form the same amount of diselenide was only 1/8 of that in neutral solution; (2) there was no foaming evolution or deleterious gas and the reaction proceeded mildly; (3) the powdered selenium could be added once; and (4) the yields of diselenides were higher.

In Eqn(2), hydrogen atoms in $NaBH_4$ are oxidised to hydrogen gas, and two molecules of $NaBH_4$ donate eight electrons, in which six electrons are consumed by forming H_2, and only two electrons reduce Se to form the Se_2^{2-} ion. Whereas, in Eqn(1), the electrons from the $NaBH_4$ all lead Se to form Se_2^{2-}, so the reduction efficiency of $NaBH_4$ is eight times in Eqn(1) as that in Eqn(2).

Thus, the added NaOH changes the reaction path. Another function of the added NaOH may be that the base can restrain the decomposition of $NaBH_4$. Whereby in our experiments, the amount of NaOH was in excess by 1/7, which kept the pH in the reactive solution at 13. Surfactant was added to the solution in order to enhance the solubility of selenium in water in our experiments.

In ethanol solution, Na_2Se_2 can be prepared by using the same molar ratio (1:8) of $NaBH_4$ to Se as in alkaline aqueous solution in the presence of sodium ethylate as suggested in Eqn(3), with no expulsion of toxic H_2Se. So there is no loss of selenium and the reduction efficiency of $NaBH_4$ is eight times that in neutral ethanol, as shown in Eqn(4). The resultant brownish red solution, stirred for 1h at room temperature with benzyl chloride, gave dibenzyl diselenide in 94% yield (lit.[7] 92%). $(i\text{-}C_3H_7Se)_2$ could also be prepared with $(CH_3)_2CHBr$ in 61% yield.

$$NaBH_4 + 8Se + 7EtONa \longrightarrow 4Na_2Se_2 + B(OEt)_3 + 4EtOH \quad (3)$$

$$2NaBH_4 + 3Se + 6EtOH \longrightarrow Na_2Se_2 + 2B(OEt)_3 + H_2Se + 6H_2 \quad (4)$$

There are some differences in preparing alkaline ethanolic solutions and aqueous solutions. First, in ethanolic solution, about 30% more EtONa is needed compared with that in aqueous solution. It may be related with the low solubility of $NaBH_4$ in ethanol. Second, there is no need to add any surfactant in ethanolic solution because the selenium powder can be easily dispersed by ethanol. For the same reason, $NaBH_4$ and selenium interact vigorously so the solution of $NaBH_4$-EtONa should be dropped into the Se-EtOH solution very slowly.

Klayman described powdered sulfur being essentially inert to the action of $NaBH_4$ in water at room temperature, but in ethanol it was reactive to form sodium hydrogen sulfide. However, we found that in the presence of base, powdered sulfur can be easily reduced with $NaBH_4$ not only in ethanol but also in water with a 8:1 molar ratio of sulfur to $NaBH_4$. So the reaction may proceed analogously in Eqn(1) (in NaOH-H_2O solution) and Eqn(3) (in NaOEt-EtOH solution). For the fact that $NaBH_4$ can reduce sulfur at the presence of base, the sole reason would be that added base changes the reaction path as described above.

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In conclusion, in the presence of sodium hydroxide or sodium ethylate, the redox reaction of selenium or sulfur with borohydride is performed by another path, differing from that in neutral solution; the reduction efficiency of $NaBH_4$ is enhanced 8 times without gas formation. Thus, sodium diselenide can be prepared conveniently and safely even on a large scale and the obtained diselenide solution can be further used directly.

Experimental

Sodium diselenide (alkaline aqueous): Selenium (3.95g, 50mmol) was added to an alkaline aqueous solution (25ml) which contained NaOH (2g) and hexadecyltrimethyl ammonium bromide in a catalytic amount. Then, to the above solution, $NaBH_4$ (0.25g, 6.6mmol) with NaOH (0.2g) in 5ml of water (cooled in an ice bath) was added in drops at room temperature under a nitrogen atmosphere with stirring. The mixture was stirred for 1h at room temperature, then raised to 90°C and stirred at this temperature for 0.5h to complete the reaction. A brownish red aqueous solution of Na_2Se_2 was obtained which could be used directly for further reaction without other treatment.

Sodium diselenide (alkaline ethanolic): Sodium metal (1.5g, 65mmol) was added to absolute ethanol (35ml). After the initial vigorous reaction had subsided, $NaBH_4$ (0.25g, 6.6mmol) was added in an ice bath. The above mixture was dropped slowly into a solution of powdered selenium (3.95g, 50mmol) dispersed in 5ml of absolute ethanol. After stirring for 1h at room temperature, the mixture was stirred for another 0.5h at 70°C to finish the reaction. Thus obtained, the brownish red alkaline ethanolic solution of Na_2Se_2 was ready for further use.

Diselenides: An alkaline solution of Na_2Se_2 prepared as described above was used directly to synthesise 2,2′-diselenodibenzoic acid, dibenzyl diselenide and bis(i-propylselenide) in fair yields respectively. These diselenides were identified by their melting or boiling points, IR spectra and ^1H NMR spectra. The results were in good accordance with the literature data.[3d, 6b, 8]

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